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SIMULTANEOUS DIOPHANTINE APPROXIMATION

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1. It is well known that for each positive integer n there exists an absolute constant $\mathbf{C}_n$ such that, for any irrational numbers $\theta_1, \theta_2, \ldots, \theta_n$, there are sets of integers $u_0, u_1, \ldots, u_n$, with u_0 arbitrarily large, satisfying

$$| u_0 \theta_r - u_r | < \left| \frac{\mathbf{C}_n}{u_0} \right|^{1/n}, \qquad r = 1, 2, \ldots, n. \tag{1}$$

Hurwitz proved that the best possible value for $\mathbf{C}_1$ is $1/\sqrt{5}$; but this is the only case in which the best possible value of $\mathbf{C}_n$ is known. Minkowski proved that (1) can always be satisfied, when

$$\mathbf{C}_n = \left(\frac{n}{n+1}\right)^n;$$

here

$$\left(\frac{n}{n+1}\right)^n \to \frac{1}{e} \text{ as } n \to \infty.$$

Blichfeldt[1] has obtained the stronger result that (1) can always be satisfied, when

$$\mathbf{C}_n = \left(\frac{n}{n+1}\right)^n \left\{1 + \left(\frac{n-1}{n+1}\right)^{n+3}\right\}^{-1};$$

here

$$\left(\frac{n}{n+1}\right)^n \left\{1 + \left(\frac{n-1}{n+1}\right)^{n+3}\right\}^{-1} \to \frac{e}{e^2+1} \text{ as } n \to \infty.$$

A related problem is that of finding, for all n, as small a constant $\mathbf{C}_n$ as possible, such that for all irrational numbers $\theta_1, \theta_2, \ldots, \theta_n$ it is possible to find sets of integers $u_0, u_1, \ldots, u_n$ with u_0 arbitrarily large such that

$$\frac{1}{n} \sum_{r=1}^{n} (u_0 \theta_r - u_r)^2 < \left(\frac{\mathbf{C}_n}{u_0}\right)^{2/n}. \tag{2}$$

Davenport and Mahler[2] have considered this problem when $n = 2$. They prove that, if $\mathbf{C}_2 \geqslant \frac{1}{(\sqrt{23})}$, then it is always possible to satisfy (2), but, if $\mathbf{C}_2 < \frac{1}{(\sqrt{23})}$, then for certain irrational numbers θ_1, θ_2, there are only a finite number of sets of integers u_0, u_1, u_2 satisfying (2). It is not difficult to show that (2) can always be satisfied with constants $\mathbf{C}_n$ which are, for

large n, very much smaller than the constants C_n for which (1) has been established. We show that the following theorem is an immediate consequence of Blichfeldt's[3] well-known inequality for the minimum of a positive definite quadratic form.

THEOREM 1.—If $\theta_1, \theta_2, \ldots, \theta_n$ are any irrational numbers, then there exist sets of integers $u_0, u_1, \ldots, u_n$, with u_0 arbitrarily large, such that

$$\frac{1}{n}\sum_{r=1}^{n}(u_0\theta_r - u_r)^2 < \left|\frac{C_n'}{u_0}\right|^{2/n}, \tag{3}$$

where

$$C_n' = \frac{\Gamma(\frac{1}{2}\{n+5\})}{(\frac{1}{2}\pi\{n+1\})^{(n+1)/2}}, \tag{4}$$

so that, as $n \to \infty$,

$$C_n' \sim \frac{n^{3/2}}{2e^{\frac{1}{2}}(\pi e)^{n/2}} = \frac{n^{3/2}}{3\cdot 297\ldots.(\pi e)^{n/2}}. \tag{5}$$

Our main object in this paper is to prove the following theorem, giving a stronger result when n is large.

THEOREM 2.—If $n > 10^7$ and $\theta_1, \theta_2, \ldots, \theta_n$ are any irrational numbers, then there exist sets of integers $u_0, u_1, \ldots, u_n$ with u_0 arbitrarily large, such that

$$\frac{1}{n}\sum_{r=1}^{n}(u_0\theta_r - u_r)^2 < \left|\frac{C_n''}{u_0}\right|^{2/n}, \tag{6}$$

where

$$C_n'' = \frac{\Gamma(\frac{1}{2}\{n+4\})}{(\frac{1}{2}\pi\{(n+2a)\})^{n/2}}\left(1 - \frac{3\cdot 3\,(\log n)^{3/2}}{\sqrt{n}}\right)^{-1}, \tag{7}$$

$$a = \sum_{k=1}^{\infty}\frac{2\log k}{(k+1)(k+2)} = 1\cdot 204635\ldots., \tag{8}$$

so that, as $n \to \infty$

$$C_n'' \sim \frac{\pi^{1/2}n^{3/2}}{2e^{a}(\pi e)^{n/2}} = \frac{n^{3/2}}{3\cdot 763\ldots.(\pi e)^{n/2}}. \tag{9}$$

We obtain this result as a consequence of the following more general theorem in the Geometry of Numbers.

THEOREM[4] 3.—Suppose that $n > 10^7$ and that $K_n^{(X)}$ is the $(n+1)$ dimensional star body defined by the inequalities

$$\left.\begin{aligned} &\frac{1}{n}\sum_{r=1}^{n} x_r^2\,|\,x_0\,|^{2/n} < 1,\\ &\frac{1}{n}\sum_{r=1}^{n} x_r^2 \qquad\quad < X^2,\\ &|\,x_0\,| \qquad\quad < 1. \end{aligned}\right\} \tag{10}$$

Then, if X is sufficiently large,

$$\Delta(K_n^{(X)}) \geqslant (C_n'')^{-1}, \tag{11}$$

where C_n'' is given by (7) and (8).

We also use Theorem 3 to prove the following theorem on Diophantine approximation, which is closely related to Theorem 2.

THEOREM 4.—If $n > 10^7$ and $\theta_1, \theta_2, \ldots, \theta_n$ are any irrational numbers $1, \theta_1, \theta_2, \ldots, \theta_n$ being linearly independent, then there exist sets of integers $u_0, u_1, \ldots, u_n$ with $u_1^2 + u_2^2 + \ldots + u_n^2$ arbitrarily large, such that

$$|u_0 - \theta_1 u_1 - \ldots - \theta_n u_n| \leqslant C_n'' \left(\frac{1}{n} \sum_{r=1}^{n} u_r^2\right)^{-n/2}, \tag{12}$$

where C_n'' is given by (7) and (8).

I am grateful to Mr. C. A. Rogers, for suggesting this investigation to me and for the advice and encouragement he has given me.

2. *Proof of Theorem* 1.—For all $\lambda > 0$, the quadratic form

$$\frac{1}{n+1}\left(\frac{u_0}{\lambda^n}\right)^2 + \frac{\lambda^2}{n+1} \sum_{r=1}^{n} (u_0\theta_r - u_r)^2$$

in the variables $u_0, u_1, \ldots, u_n$ has determinant $(n+1)^{-(n+1)}$. So by Blichfeldt's result[4] it is possible to find integers $u_0, u_1, \ldots, u_n$ not all zero, satisfying

$$\frac{1}{n+1}\left(\frac{u_0}{\lambda^n}\right)^2 + \frac{\lambda^2}{n+1} \sum_{r=1}^{n} (u_0\theta_r - u_r)^2 \leqslant \frac{[\Gamma(\frac{1}{2}\{n+5\})]^{2/(n+1)}}{\frac{1}{2}\pi(n+1)}. \tag{13}$$

As $\theta_1, \theta_2, \ldots, \theta_n$ are irrational and $u_0, u_1, \ldots, u_n$ are not all zero it follows from (13) that u_0 will be arbitrarily large if λ is arbitrarily large. Further, using the inequality of the arithmetic and geometric means and (13), we have

$$\begin{aligned} |u_0|^{2/n} \frac{1}{n} \sum_{r=1}^{n} (u_0\theta_r - u_r)^2 &< \left\{\frac{1}{n+1}\left(\frac{u_0}{\lambda^n}\right)^2 + \frac{\lambda^2}{n+1} \sum_{r=1}^{n} (u_0\theta_r - u_r)^2\right\}^{(n+1)/n} \\ &\leqslant \frac{\{\Gamma(\frac{1}{2}\{n+5\})\}^{2/n}}{\{\frac{1}{2}\pi(n+1)\}^{(n+1)/n}}. \end{aligned}$$

This proves that there are sets of integers $u_0, u_1, \ldots, u_n$ with u_0 arbitrarily large, satisfying (3) where C_n' is given by (4). The result (5) follows from (4) by use of Stirling's formula.

3. Before we can prove Theorem 3, we need a series of lemmas. The first of these is a statement of a well-known result due to Blichfeldt.

Lemma 1. Suppose $\rho(x_1, x_2, \ldots, x_n)$ is a non-negative function which is integrable in the Lebesgue sense and which vanishes outside a bounded region. Suppose Λ is a lattice of determinant Δ and that for all points $(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_n)$ of space

$$\Sigma\rho(\bar{x}_1 - x_1, \bar{x}_2 - x_2, \ldots, \bar{x}_n - x_n) \leqslant \rho_0, \tag{14}$$

the sum being taken over all the lattice points $(x_1, x_2, \ldots, x_n)$ of Λ. Then

$$\rho_0 \Delta \geqslant \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \rho(\xi_1, \xi_2, \ldots, \xi_n)\, d\xi_1\, d\xi_2 \ldots d\xi_n. \tag{15}$$

Proof.—It is clear that we may suppose without loss of generality that $\Delta = 1$ and that Λ is the lattice of points with integral co-ordinates. Then, using (14), we have

$$\begin{aligned}
&\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} \rho(\xi_1, \xi_2, \ldots, \xi_n)\, d\xi_1\, d\xi_2 \ldots d\xi_n \\
&= \Sigma \int_0^1\int_0^1 \ldots \int_0^1 \rho(\xi_1 - x_1, \xi_2 - x_2, \ldots, \xi_n - x_n)\, d\xi_1\, d\xi_2 \ldots d\xi_n \\
&= \int_0^1\int_0^1 \ldots \int_0^1 \Sigma\rho(\xi_1 - x_1, \xi_2 - x_2, \ldots, \xi_n - x_n)\, d\xi_1\, d\xi_2 \ldots d\xi_n \\
&\leqslant \int_0^1\int_0^1 \ldots \int_0^1 \rho_0\, d\xi_1\, d\xi_2 \ldots d\xi_n = \rho_0 = \rho_0\, \Delta,
\end{aligned}$$

where the sums are taken over all the points $(x_1, x_2, \ldots, x_n)$ with integral co-ordinates. This proves the lemma.

Our next lemma is also due to Blichfeldt.[5]

Lemma 2.—Suppose that, in n-dimensional space, $(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_n)$ is any given point and $(x_1^{(r)}, x_2^{(r)}, \ldots, x_n^{(r)})$. $r = 1, 2, \ldots, m$, are any other m points. Then

$$\begin{aligned}
&m \sum_{r=1}^{m} \{(x_1^{(r)} - \bar{x}_1)^2 + \ldots + (x_n^{(r)} - \bar{x}_n)^2\} \\
&\geqslant \sum_{1 \leqslant r < s \leqslant m}^{r,\,s} \{(x_1^{(r)} - x_1^{(s)})^2 + \ldots + (x_n^{(r)} - x_n^{(s)})^2\}
\end{aligned} \tag{16}$$

Proof.—We have

$$\begin{aligned}
&m \sum_{r=1}^{m} (x_k^{(r)} - \bar{x}_k)^2 \\
&\geqslant m \sum_{r=1}^{m} (x_k^{(r)} - \bar{x}_k)^2 - \{\sum_{r=1}^{m} (x_k^{r} - \bar{x}_k)\}^2
\end{aligned}$$

$$= (m-1)\sum_{r=1}^{m}(x_k^{(r)}-\bar{x}_k)^2 - 2\sum_{1\leqslant r<s\leqslant m}^{r,s}(x_k^{(r)}-\bar{x}_k)(x_k^{(s)}-\bar{x}_k)$$

$$= \sum_{1\leqslant r<s\leqslant m}^{r,s}\{(x_k^{(r)}-\bar{x}_k)-(x_k^{(s)}-\bar{x}_k)\}^2$$

$$= \sum_{1\leqslant r<s\leqslant m}^{r,s}(x^{(r)}{}_k - x^{(s)}{}_k)^2,$$

for $k = 1, 2, \ldots, n$. Summing over k we obtain (16).

4. The next lemma is rather more difficult; it is by use of this lemma that we are able to improve on the result of Theorem 1.

Lemma 3.—Suppose that $m \geqslant 2$ and that $\bar{z}, z_1, z_2, \ldots, z_m$ are real numbers satisfying

$$z_1 < z_2 < \ldots < z_m \tag{17}$$

and

$$|z - z_r| \leqslant \tfrac{1}{2} \text{ for } r = 1, 2, \ldots, m \tag{18}$$

Then

$$\sum_{1\leqslant r<s\leqslant m}^{r,s}|z_r - z_s|^{-2/n} \geqslant \tfrac{1}{2}m(m-1) + \sum_{6\leqslant (k+1)(k+2)\leqslant \frac{3}{2}m} k(k^{2/n}-1)\frac{2m^2-3(k+1)(k+2)m}{2k(k+1)(k+2)}. \tag{19}$$

Further, if $m \geqslant 160$,

$$\sum_{6\leqslant (k+1)(k+2)\leqslant \frac{3}{2}m} k(k^{2/n}-1)\frac{2m^2-3(k+1)(k+2)m}{2k(k+1)(k+2)} \geqslant \frac{m^2}{n}\sum_{k=1}^{\infty}\frac{2\log k}{(k+1)(k+2)} - \frac{3m\sqrt{m}\log m}{n} > 0. \tag{20}$$

Proof.—Rearranging the sum on the left of (19) we obtain

$$\sum_{1\leqslant r<s\leqslant m}|z_r - z_s|^{-2/n} = \sum_{d=1}^{m-1}\left\{\sum_{a=1}^{m-d}|z_{a+d}-z_a|^{-2/n}\right\} = \sum_{d=1}^{m-1}\left\{\sum_{a=1}^{\min\{d,m-d\}}\sum_{r=1}^{\left[\frac{m-a}{d}\right]}|z_{a+rd}-z_{a+(r-1)d}|^{-2/n}\right\}. \tag{21}$$

But using Holder's well-known inequality and (17) and (18), we have

$$\sum_{r=1}^{\left[\frac{m-a}{d}\right]}|z_{a+rd}-z_{a+(r-1)d}|^{-2/n}$$

$$> \left(\left[\frac{m-a}{d}\right]\right)^{1+(2/n)} \left\{ \sum_{r=1}^{\left[\frac{m-a}{d}\right]} | z_{a+rd} - z_a | \right\}^{-2/n}$$

$$= \left(\left[\frac{m-a}{d}\right]\right)^{1+(2/n)} \left| z_a + \left[\frac{m-a}{d}\right] d - z_a \right|^{-2/n}$$

$$> \left(\left[\frac{m-a}{d}\right]\right)^{1+(2/n)}. \tag{22}$$

So, by (21) and (22)

$$\sum_{1 \leqslant r < s \leqslant m}^{r, s} | z_r - z_s |^{-2/n}$$

$$> \sum_{d=1}^{m-1} \sum_{a=1}^{\min\{d, m-d\}} \left(\left[\frac{m-a}{d}\right]\right)^{1+(2/n)}$$

$$= \sum_{d=1}^{m-1} \sum_{a=1}^{\{\min d, m-d\}} \left[\frac{m-a}{d}\right]$$

$$+ \sum_{d=1}^{m-1} \sum_{a=1}^{\min\{d, m-d\}} \left[\frac{m-a}{d}\right] \left\{ \left[\frac{m-a}{d}\right]^{2/n} - 1 \right\}. \tag{23}$$

Reversing the steps which led to (21) we obtain

$$\sum_{d=1}^{m-1} \sum_{a=1}^{\min\{d, m-d\}} \left[\frac{m-a}{d}\right] = \sum_{1 \leqslant r < s \leqslant m}^{r, s} 1 = \tfrac{1}{2} m (m-1). \tag{24}$$

We now have to estimate the second sum on the right of (23). It will be convenient to collect together all the terms of the sum for which $\left[\frac{m-a}{d}\right]$ has a definite integral value. Let $r(k, m)$ be the number of pairs of integers a, d satisfying

$$\left.\begin{aligned} &\left[\frac{m-a}{d}\right] = k, \\ &1 \leqslant d \leqslant m-1, \\ &1 \leqslant a \leqslant \min\{d, m-d\}, \end{aligned}\right\} \tag{25}$$

so that

$$\sum_{d=1}^{m-1} \sum_{a=1}^{\min\{d\, m-d\}} \left[\frac{m-a}{d}\right] \left\{ \left[\frac{m-a}{d}\right]^{2/n} - 1 \right\}$$

$$= \sum_{k=1}^{m-1} r(k, m)\, k\, (k^{2/n} - 1). \tag{26}$$

But, if $k > 1$, $m > 1$, it is clear that a, d will satisfy (25) if and only if the satisfy

$$\begin{cases} 1 \leqslant d \leqslant m-1, \\ m-(k+1)\,d < a \leqslant m-kd, \\ 1 \leqslant a \leqslant \min\{d, m-d\}; \end{cases}$$

i.e., if and only if they satisfy

$$\begin{cases} 1 \leqslant d \leqslant m-1, \\ (m-kd)-d < a \leqslant m-kd, \\ 0 < a \leqslant d; \end{cases}$$

i.e., if and only if they satisfy

$$\text{either} \begin{cases} 1 \leqslant d \leqslant m-1, \\ 0 \leqslant m-kd < d, \\ 0 < a \leqslant m-kd \end{cases} \text{ or } \begin{cases} 1 \leqslant d \leqslant m-1 \\ d \leqslant m-kd < 2d, \\ (m-kd)-d < a \leqslant d; \end{cases}$$

i.e., if and only if they satisfy

$$\text{either} \begin{cases} 1 \leqslant d \leqslant m-1, \\ \dfrac{m}{k+1} < d \leqslant \dfrac{m}{k}, \\ 0 < a \leqslant m-kd, \end{cases} \text{ or } \begin{cases} 1 \leqslant d \leqslant m-1, \\ \dfrac{m}{k+2} < d \leqslant \dfrac{m}{k+1}, \\ 0 \leqslant d-a < (k+2)\,d-m; \end{cases}$$

i.e., if and only if they satisfy

$$\text{either} \begin{cases} \left[\dfrac{m}{k+1}\right]+1 \leqslant d \leqslant \left[\dfrac{m}{k}\right], \\ 0 < a \leqslant m-kd, \end{cases} \text{ or } \begin{cases} \left[\dfrac{m}{k+2}\right]+1 \leqslant d \leqslant \dfrac{m}{k+1}\Big], \\ 0 \leqslant d-a < (k+2)\,d-m; \end{cases} \tag{27}$$

Since it is not possible for a and d to satisfy both the alternatives in (27), it follows that, if $k > 1$, $m > 1$, then

$$\begin{aligned} r(k,m) &= \sum_{d=\left[\frac{m}{k+1}\right]+1}^{\left[\frac{m}{k}\right]} \sum_{a=1}^{m-kd} 1 + \sum_{d=\left[\frac{m}{k+2}\right]+1}^{\left[\frac{m}{k+1}\right]} \sum_{a=0}^{(k+2)d-m-1} 1, \\ &= \sum_{d=\left[\frac{m}{k+1}\right]+1}^{\left[\frac{m}{k}\right]} (m-kd) + \sum_{d=\left[\frac{m}{k+2}\right]+1}^{\left[\frac{m}{k+1}\right]} \{(k+2)\,d-m\} \\ &= \tfrac{1}{2}\left\{\left[\frac{m}{k}\right]-\left[\frac{m}{k+1}\right]\right\}\left\{2m-\left(\left[\frac{m}{k}\right]+\left[\frac{m}{k+1}\right]+1\right)k\right\} \end{aligned}$$

$$+\tfrac{1}{2}\left\{\left[\frac{m}{k+1}\right]-\left[\frac{m}{k+2}\right]\right\}\left\{\left(\left[\frac{m}{k+1}\right]+\left[\frac{m}{k+2}\right]+1\right)(k+2)-2m\right\}$$

$$\geqslant \tfrac{1}{2}\left\{\left[\frac{m}{k}\right]-\left[\frac{m}{k+1}\right]\right\}\left\{2m-\left(\frac{m}{k}+\frac{m}{k+1}+1\right)k\right\}$$

$$+\tfrac{1}{2}\left\{\left[\frac{m}{k+1}\right]-\left[\frac{m}{k+2}\right]\right\}\left\{\left(\frac{m}{k+1}+\frac{m}{k+2}-1\right)(k+2)-2m\right\}$$

$$=\tfrac{1}{2}\left\{\left[\frac{m}{k}\right]-\left[\frac{m}{k+1}\right]\right\}\left\{\frac{m}{k+1}-k\right\}$$

$$+\tfrac{1}{2}\left\{\left[\frac{m}{k+1}\right]-\left[\frac{m}{k+2}\right]\right\}\left\{\frac{m}{k+1}-(k+2)\right\}$$

$$\geqslant \tfrac{1}{2}\left\{\left[\frac{m}{k}\right]-\left[\frac{m}{k+2}\right]\right\}\left\{\frac{m}{k+1}-(k+2)\right\}.$$

Provided

$$(k+1)(k+2<\tfrac{2}{3}m,$$

we have

$$r(k,m)\geqslant \tfrac{1}{2}\left\{\left[\frac{m}{k}\right]-\left[\frac{m}{k+2}\right]\right\}\left\{\frac{m-(k+1)(k+2)}{(k+1)}\right\}$$

$$\geqslant \tfrac{1}{2}\left\{\frac{m}{k}-\frac{m}{k+2}-1\right\}\left\{\frac{m-(k+1)(k+2)}{k+1}\right\}$$

$$=\frac{\{2m-k(k+2)\}\{m-(k+1)(k+2)\}}{2k(k+1)(k+2)}$$

$$>\frac{2m^2-3(k+1)(k+2)m}{2k(k+1)(k+2)}>0. \tag{27}$$

Thus, by (26) and (27),

$$\sum_{d=1}^{m-1}\sum_{a=1}^{\min\{d,m-d\}}\left[\frac{m-a}{d}\right]\left\{\left[\frac{m-a}{d}\right]^{2/n}-1\right\}$$

$$\geqslant \sum_{6\leqslant (k+1)(k+2)\leqslant \frac{2}{3}m} k(k^{2/n}-1)\frac{2m^2-3(k+1)(k+2)m}{2k(k+1)(k+2)}. \tag{28}$$

Now (19) follows from (23), (24) and (28).

To prove the last clause of the lemma we suppose that $m\geqslant 160$ and use the elementary inequality

$$k^{2/n}-1\geqslant\frac{2}{n}\log k,\qquad (k\geqslant 1).$$

We have

$$\sum_{6\leqslant (k+1)(k+2)\leqslant \frac{2}{3}m} k(k^{2/n}-1)\frac{2m^2-3(k+1)(k+2)m}{2k(k+1)(k+2)}$$

$$\geqslant \sum_{6\leqslant (k+1)(k+2)\leqslant \frac{2}{3}m}\frac{2}{n}\log k\,\frac{2m^2-3(k+1)(k+2)m}{2(k+1)(k+2)}$$

$$\geqslant \sum_{6 \leqslant (k+1)(k+2) \leqslant (\sqrt{m}+1)(\sqrt{m}+2)} \frac{\log k}{n} \cdot \frac{2m^2 - 3(k+1)(k+2)m}{(k+1)(k+2)}$$

$$= \frac{m^2}{n} \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - \frac{m^2}{n} \sum_{k \geqslant \sqrt{m}} \frac{2 \log k}{(k+1)(k+2)}$$

$$- \frac{3m}{n} \sum_{1 \leqslant k < \sqrt{m}} \log k$$

$$\geqslant \frac{m^2}{n} \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - \frac{m^2}{n} \sum_{k \geqslant \sqrt{m}} \frac{2 \log k}{(k+1)(k+2)}$$

$$- \frac{3m}{n} \sqrt{m} \log \sqrt{m}. \tag{29}$$

Now

$$\frac{\log k}{(k+1)(k+2)} = \frac{\log k}{k+1} - \frac{\log (k+1)}{k+2} + \frac{\log (1 + 1/k)}{k+2}$$

$$< \frac{\log k}{k+1} - \frac{\log (k+1)}{k+2} + \frac{1}{k(k+2)}$$

$$= \frac{\log k}{k+1} + \frac{1}{2k} + \frac{1}{2(k+1)}$$

$$- \frac{\log (k+1)}{k+2} - \frac{1}{2(k+1)} - \frac{1}{2(k+2)},$$

so that

$$\sum_{k \geqslant \sqrt{m}} \frac{2 \log k}{(k+1)(k+2)} < \frac{2 \log \sqrt{m}}{\sqrt{m}+1} + \frac{1}{\sqrt{m}} + \frac{1}{(\sqrt{m}+1)}$$

$$< \frac{2 + 2 \log \sqrt{m}}{\sqrt{m}} \tag{30}$$

Hence, by (29) and (30), the sum on the left-hand side of (29) does not exceed

$$\frac{m^2}{n} \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - \frac{2m^2(1 + \log \sqrt{m})}{n\sqrt{m}} - \frac{3m\sqrt{m} \log \sqrt{m}}{n}$$

$$= \frac{m^2}{n} \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - \frac{m\sqrt{m}(2 + 2 \cdot \frac{1}{2} \log m)}{n}$$

$$> \frac{m^2}{n} \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - \frac{3m\sqrt{m} \log m}{n} > 0,$$

using our assumption that $m \geqslant 160$ and the numerical result

$$\sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} = 1 \cdot 204635\ldots. \tag{31}$$

(This series does not converge very rapidly; but the sum can be found quite easily by use of the formula

$$\sum_{k=1}^{\infty} \frac{2\log k}{(k+1)(k+2)} = \sum_{k=1}^{l-1} \frac{2\log k}{(k+1)(k+2)} + \frac{2l\log l + 2l + 1}{l(l+1)} - \sum_{k=1}^{\infty} \frac{2}{k+1}\left\{\log\left(1-\frac{1}{k+1}\right) + \frac{1}{k+1} + \frac{1}{2k(k+1)}\right\},$$

for a suitable value of l.)

This completes the proof of the lemma.

5. *Proof of Theorem* 3.—Suppose that $n > 10^7$ and that $\mathbf{X}$ is sufficiently large. Let Λ be any $(n+1)$-dimensional lattice with determinant Δ and with no point other than the origin in the interior of the body $k_n^{(X)}$. We have to prove that

$$\Delta \geqslant 1/C_n'', \tag{32}$$

where C_n'' is given by (7) and (8).

We write

$$a = \sum_{k=1}^{\infty} \frac{2\log k}{(k+1)(k+2)}, \tag{33}$$

$$R = \left\{\frac{n}{2} + a - \frac{3(\log n)^{3/2}}{\sqrt{n}}\right\}^{\frac{1}{2}}, \tag{34}$$

and we define $\rho(x_0, x_1, \ldots, x_n)$, by

$$\rho(x_0, x_1, \ldots, x_n) = R^2 - x_1^2 - \ldots - x_n^2, \tag{35}$$

if both

$$|x_0| < \tfrac{1}{2} \tag{36}$$

and

$$R^2 - \tfrac{1}{2}\log n \leqslant x_1^2 + \ldots + x_n^2 < R^2; \tag{37}$$

and by

$$\rho(x_0, x_1, \ldots, x_n) = 0 \tag{38}$$

otherwise.

Our first object is to prove that the function ρ satisfies a condition like condition (14) of Lemma 1. It is clear that for all $x_0, x_1, \ldots, x_n$, we have

$$0 \leqslant \rho(x_0, x_1, \ldots, x_n) \leqslant \tfrac{1}{2}\log n. \tag{39}$$

Suppose $(\bar{x}_0, \bar{x}_1, \ldots, \bar{x}_n)$ is any point of space, and consider the sum

$$\Sigma\rho(\bar{x}_0 - x_0, \bar{x}_1 - x_1, \ldots, \bar{x}_n - x_n) \tag{40}$$

taken over all the lattice points $(x_0, x_1, \ldots, x_n)$ of Λ. This sum is equal to

$$\sum_{r=1}^{m} \rho(\bar{x}_0 - x_0^{(r)}, \bar{x}_1 - x_1^{(r)}, \ldots, \bar{x}_n - x_n^{(r)}) \tag{41}$$

where $(x_0^{(r)}, x_1^{(r)}, \ldots, x_n^{(r)})$, $r = 1, 2, \ldots, m$ are the points of $\wedge$, for which

$$\rho(\bar{x}_0 - x_0^{(r)}, \bar{x}_1 - x_1^{(r)}, \ldots, \bar{x}_n - x_n^{(r)}) > 0 \tag{42}$$

If $m \leqslant n/(\log n)$, it follows immediately from (39) that

$$\sum_{r=1}^{m} \rho(\bar{x}_0 - x_0^{(r)}, \bar{x}_1 - x_1^{(r)}, \ldots, \bar{x}_n - x_n^{(r)}) \leqslant \tfrac{1}{2}n \tag{43}$$

We now consider the case when $m > n/(\log n)$. Then, by our supposition concerning n,

$$m > 160 \tag{44}$$

It follows from (42) and the definition of $\rho(x_0, x_1, \ldots, x_n)$ that

$$|\bar{x}_0 - x_0^{(r)}| < \tfrac{1}{2}, \tag{45}$$

and

$$(\bar{x}_1 - x_1^{(r)})^2 + \ldots + (\bar{x}_n - x_n^{(r)})^2 < \mathrm{R}^2, \tag{46}$$

for $r = 1, 2, \ldots, m$. Thus, if $1 \leqslant r < s \leqslant m$,

$$|x_0^{(r)} - x_0^{(s)}| < 1 \tag{47}$$

and

$$(x_1^{(r)} - x_1^{(s)})^2 + \ldots + (x_n^{(r)} - x_n^{(s)})^2 > 4\mathrm{R}^2 \tag{48}$$

since $(x_1^{(r)}, x_2^{(r)}, \ldots, x_n^{(r)})$ and $(x_1^{(s)}, x_2^{(s)}, \ldots, x_n^{(s)})$ are two distinct lattice points of $\wedge$, the point $(x_1^{(r)} - x_1^{(s)}, x_2^{(r)} - x_2^{(s)}, \ldots, x_n^{(r)} - x_n^{(s)})$ being a point other than O of $\wedge$, is not in the interior of the body $k_n(\mathrm{X})$. Provided X is so large that $\mathrm{X}^2 \geqslant 4n\mathrm{R}^2$ it follows from (47), (48) and the definition of $k_n(\mathrm{X})$ that

$$\sum_{k=1}^{n} (x_k^{(r)} - x_k^{(s)})^2 |x_0^{(r)} - x_0^{(s)}|^{2/n} \geqslant n, \tag{49}$$

if $1 \leqslant r < s \leqslant m$. Thus, by Lemma 2,

$$\begin{aligned} m \sum_{r=1}^{m} &\{(x_1^{(r)} - \bar{x}_1)^2 + \ldots + (x_n^{(r)} - \bar{x}_n)^2\} \\ &\geqslant \sum_{1 \leqslant r < s \leqslant m}^{r,s} \{(x_1^{(r)} - x_1^{(s)})^2 + \ldots + (x_n^{(r)} - x_n^{(s)})^2\} \\ &\geqslant n \sum_{1 \leqslant r < s \leqslant m}^{r,s} |x_0^{(r)} - x_0^{(s)}|^{-2/n}. \end{aligned} \tag{50}$$

Let $z_1, z_2, \ldots, z_m$ be the numbers $x_0^{(1)}, x_0^{(2)}, \ldots, x_0^{(m)}$ arranged in order of magnitude and write $\bar{z} = \bar{x}_0$. Then by (44) and (45), the conditions of Lemma 3 are satisfied. Consequently, by Lemma 3 and (50)

$$m \sum_{r=1}^{m} \{(x_1^{(r)} - \bar{x}_1)^2 + \ldots + (x_n^{(r)} - \bar{x}_n)^2\}$$

$$\geqslant n \sum_{1 \leqslant r < s \leqslant m}^{r,s} | x_0^{(r)} - x_0^{(s)} |^{-2/n}$$

$$= n \sum_{1 \leqslant r < s \leqslant m}^{r,s} | z_r - z_s |^{-2/n}$$

$$\geqslant \tfrac{1}{2} m (m-1) n + m^2 \sum_{k=1}^{\infty} \frac{2 \log k}{(k+1)(k+2)} - 3m\sqrt{m} \log m.$$

Using our supposition that $m > n/(\log n)$ and (33) and (34), this gives

$$\sum_{r=1}^{m} \{(x_1^{(r)} - \bar{x}_1)^2 + \ldots + (x_n^{(r)} - \bar{x}_n)^2\}$$

$$\geqslant \tfrac{1}{2} (m-1) n + am - m \frac{3 \log \{n/(\log n)\}}{\{n \log n\}^{\frac{1}{2}}}$$

$$\geqslant \tfrac{1}{2} (m-1) n + am - \frac{3m (\log n)^{3/2}}{\sqrt{n}}$$

$$= m\mathrm{R}^2 - \tfrac{1}{2} n.$$

Hence, by the definition of $\rho(x_0, x_1, \ldots, x_n)$, and (46),

$$\sum_{r=1}^{m} \rho(\bar{x}_0 - x_0^{(r)}, \bar{x}_1 - x_1^{(r)}, \ldots, \bar{x}_n - x_n^{(r)})$$

$$\leqslant \sum_{r=1}^{m} \{\mathrm{R}^2 - (x_1^{(r)} - \bar{x}_1)^2 - \ldots - (x_n^{(r)} - \bar{x}_n)^2\}$$

$$\leqslant \tfrac{1}{2} n. \qquad (51)$$

Thus, by (43) and (51), it follows that in any case the sum (40) does not exceed $\frac{1}{2} n$. Since $\rho(x_0, x_1, \ldots, x_n)$ is a non-negative function which is integrable in the Lebesgue sense and which vanishes outside a bounded region, it follows by Lemma 1 that

$$\tfrac{1}{2} n \Delta \geqslant \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \rho(\xi_0, \xi_1, \ldots, \xi_n)\, d\xi_0\, d\xi_1 \ldots d\xi_n \qquad (52)$$

Now, by the definition of $\rho(x_0, x_1, \ldots, x_n)$,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \rho(\xi_0, \xi_1, \ldots, \xi_n)\, d\xi_0\, d\xi_1 \ldots d\xi_n$$

$$= \int_{-\frac{1}{2}}^{\frac{1}{2}} d\xi_0 \int_{\log \sqrt{n}\}}^{\mathrm{R}} (\mathrm{R}^2 - r^2)\, d\mathrm{J}_n r^n, \qquad (53)$$

where

$$J_n = \frac{(\pi)^{n/2}}{\Gamma(1 + \frac{1}{2}n)}, \tag{54}$$

is the volume of an n-dimensional sphere of unit radius. Using (52) and (53) and integrating

$$\begin{aligned}
\Delta &> \frac{2}{n}\left[J_n R^2 r^n - \frac{n}{n+2} J_n r^{n+2}\right]_{\sqrt{\{R^2 - \log \sqrt{n}\}}}^{R} \\
&= \frac{2J_n}{n}\left\{R^{n+2} - \frac{n}{n+2} R^{n+2} - R^2 (R^2 - \tfrac{1}{2}\log n)^{n/2}\right. \\
&\qquad \left. + \frac{n}{n+2} (R^2 - \tfrac{1}{2}\log n)^{(n+2)/2}\right\} \\
&= \frac{2J_n}{n}\left\{\frac{2}{n+2} R^{n+2} - \left(\frac{2R^2}{n+2} + \frac{\frac{1}{2}n \log n}{n+2}\right)(R^2 - \tfrac{1}{2}\log n)^{n/2}\right\} \\
&= \frac{4J_n R^{n+2}}{n(n+2)}\left\{1 - \left(1 + \frac{n \log n}{4R^2}\right)\left(1 - \frac{\log n}{2R^2}\right)^{n/2}\right\}.
\end{aligned} \tag{55}$$

Now, since by (34), and our supposition that $n \geqslant 10^7$,

$$\tfrac{1}{2}n < R^2 < \tfrac{1}{2}n + a,$$

it follows that

$$\begin{aligned}
&1 - \left(1 + \frac{n \log n}{4R^2}\right)\left(1 - \frac{\log n}{2R^2}\right)^{n/2} \\
&\geqslant 1 - (1 + \tfrac{1}{2}\log n)\left(1 - \frac{\log n}{n + 2a}\right)^{n/2} \\
&\geqslant 1 - (1 + \tfrac{1}{2}\log n)\ \exp\left(-\frac{n \log n}{2(n + 2a)}\right) \\
&\geqslant 1 - (1 + \tfrac{1}{2}\log n)\ \exp\left(-\tfrac{1}{2}\log n + \frac{2a \log n}{n}\right) \\
&\geqslant 1 - (1 + \tfrac{1}{2}\log n)\frac{1}{\sqrt{n}} \exp.\left(\frac{2a \log n}{n}\right) \\
&\geqslant 1 - \frac{\log n}{\sqrt{n}}.
\end{aligned} \tag{56}$$

Also, by (34) and our supposition that $n \geqslant 10^7$,

$$\begin{aligned}
R^{n+2} &= \left(\frac{n}{2} + a - \frac{3(\log n)^{3/2}}{\sqrt{n}}\right)^{(n+2)/2} \\
&= \left(\frac{n}{2}\right)^{(n+2)/2}\left(1 + \frac{2a}{n} - 6\left(\frac{\log n}{n}\right)^{3/2}\right)^{(n+2)2}
\end{aligned}$$

$$> \left(\frac{n}{2}\right)^{(n+2)/2} \left(1 + \frac{2a}{n}\right)^{n/2} \left(1 - 6\left(\frac{\log n}{n}\right)^{3/2}\right)^{n/2}$$

$$> \tfrac{1}{2}n\,(\tfrac{1}{2}n + a)^{n/2} \left(1 - 3n\left(\frac{\log n}{n}\right)^{3/2}\right). \tag{57}$$

Thus, by (55), (56) and (57),

$$\Delta \geqslant \frac{2J_n}{n+2}\,(\tfrac{1}{2}n + a)^{n/2} \left(1 - \frac{3\,(\log n)^{3/2}}{\sqrt{n}}\right)\left(1 - \frac{\log n}{\sqrt{n}}\right)$$

$$\geqslant \frac{2J_n}{n+2}\,(\tfrac{1}{2}n + a)^{n/2} \left(1 - \frac{3\cdot 3\,(\log n)^{3/2}}{\sqrt{n}}\right) > 0. \tag{58}$$

Now, by (54)

$$\frac{2J_n}{n+2} = \frac{(\pi)^{n/2}}{(1 + \frac{1}{2}n)\Gamma(1 + \frac{1}{2}n)} = \frac{(\pi)^{n/2}}{\Gamma(\frac{1}{2}\{n+4\})}, \tag{59}$$

and hence, using (58), (59) and (7)

$$\Delta \geqslant (C_n'')^{-1} \tag{60}$$

where C_n'' is given by (7) and (8). As we have established (60) for all lattices $\wedge$ with determinant Δ and with no lattice point other than 0 in the interior of the body $K_n^{(X)}$, it follows by the definition of $\Delta\,(K_n^{(X)})$ that

$$\Delta\,(K_n^{(X)}) \geqslant (C_n'')^{-1}.$$

This proves the theorem.

6. *Proof of Theorems* 2 *and* 4.—Suppose that $n \geqslant 10^7$ and that $\theta_1, \theta_2, \ldots, \theta_n$ are any irrational numbers. Then for any $\lambda > 0$ the lattice given by

$$x_0 = u_0\lambda^n$$

$$x_r = (u_r - \theta_r u_0)\,\lambda^{-1},\ r = 1, 2, \ldots, n,$$

has determinant 1. Hence, by Theorem 3, there are integers $u_0, u_1, \ldots, u_n$ not all zero, satisfying

$$\frac{1}{n}\sum_{r=1}^{n} x_r^2 \mid x_0 \mid^{2/n} \leqslant (C_n'')^{2/n}$$

$$\frac{1}{n}\sum_{r=1}^{n} x_r^2 \leqslant (C_n'')^{2/(n+1)}\,X^2,$$

i.e., satisfying

$$\frac{1}{n}\sum_{r=1}^{n} (u_0\theta_r - u_r)^2 \leqslant \left|\frac{C_n''}{u_0}\right|^{2/n}, \tag{61}$$

$$\frac{1}{n}\sum_{r=1}^{n} (u_0\theta_r - u_r)^2 \leqslant (C_n'')^{2/(n+1)}\,X^2\lambda^2. \tag{62}$$

Since $\theta_1, \theta_2, \ldots, \theta_n$ are irrational, it follows from (62) that u_0 will be arbitrarily large if λ is arbitrarily small. This proves Theorem 2.

A similar consideration of the lattice given by

$$x_0 = (u_0 - \theta_1 u_1 - \ldots - \theta_n u_n)\lambda^n$$
$$x_r = u_r \lambda^{-1}, \ldots, r = 1, 2, \ldots, n,$$

shows that for all $\lambda > 0$ there are integers $u_0, u_1, \ldots, u_n$ not all zero satisfying

$$| u_0 - \theta_1 u_1 - \ldots - \theta_n u_n | \leq C_n \left(\frac{1}{n} \sum_{r=1}^{n} u_r^2\right)^{-n/2} \tag{63}$$

$$| u_0 - \theta_1 u_1 - \ldots - \theta_n u_n | \leq (C_n)^{1/n+2} \lambda^{-n}. \tag{64}$$

Provided $1, \theta_1, \theta_2, \ldots, \theta_n$ are linearly independent it follows from (64) that $u_1^2 + u_2^2 + \ldots + u_n^2$ is arbitrarily large when λ is arbitrarily large. This proves Theorem 4.

This work was done by me while I was a research scholar under Prof. H. Davenport, University College, London.

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ON THE INVARIANT RELATION BETWEEN TWO COGNATE SEXTACTIC CONICS OF A CUBIC

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1. A bicursal cubic Γ possesses in general (i) 9 points of inflexion $\{I_r\}$ and 9 associated harmonic polars $\{L_r\}$, and (ii) 27 sextactic points, lying three by three on the nine harmonic polars $\{L_r\}$. To each point of inflexion I_r, there correspond three sextactic points (P_r, Q_r, R_r) which lie on the corresponding harmonic polar L_r and have I_r for their common tangential. These three sextactic points will be said to be *cognate to one another*, and their associated osculating (*i.e.*, sixpointic) conics will be similarly called *mutually cognate*. The cubic Γ has thus 9 triads of cognate sextactic points and 9 corresponding triads of cognate sextactic conics.

The present paper has for its main objective the discussion of the invariant relation, (expressed in terms of the associated invariants Δ, Δ', Θ, Θ'), that must hold between two given conics (S, S') in order that there may exist a cubic for which these are cognate sextactic conics.

Section I

Canonical Forms of a Triad of Cognate Sextactic Conics of a Cubic

2. Choose one of the inflexions of a given bicursal cubic Γ as the origin O of Cartesian co-ordinates, and the tangent to Γ at O as the x-axis. Let α be the point of contact of one of the three tangents that can be drawn to Γ from O, so that α is one of the three sextactic points lying on the harmonic polar L of O. Choose Oα as the y-axis, and let the osculating conic S at α be

$$S \equiv ax^2 + 2hxy + by^2 + 2gx + 2fy + c = 0,$$

where $$A \equiv bc - f^2 = 0. \tag{1}$$

The equation to Γ can then be presented in the form

$$Sy - x^3 = 0. \tag{2}$$

Writing this as

$$(S + 3\lambda x^2 + 3\lambda^2 xy + \lambda^3 y^2)\, y - (x + \lambda y)^3 = 0,$$

and introducing the condition that the line $x + \lambda y = 0$ should touch the conic

$$S + 3\lambda x^2 + 3\lambda^2 xy + \lambda^3 y^2 = 0,$$

we readily obtain

(i) the sextactic points β, γ cognate with α, *viz.*,

$$\left(\frac{\lambda_1}{f - \lambda_1 g}, \quad -\frac{1}{f - \lambda_1 g}\right) \text{ and } \left(\frac{\lambda_2}{f - \lambda_2 g}, \quad -\frac{1}{f - \lambda_2 g}\right), \tag{3}$$

and

(ii) the associated osculating conics

$$\left.\begin{aligned} S_1 &\equiv S + 3\lambda_1 x^2 + 3\lambda_1^2 xy + \lambda_1^3 y^2 = 0 \\ S_2 &\equiv S + 3\lambda_2 x^2 + 3\lambda_2^2 xy + \lambda_2^3 y^2 = 0, \end{aligned}\right\} \tag{4}$$

where λ_1, λ_2 are the roots of the quadratic

$$c\lambda^2 + B\lambda + 2H = 0. \tag{5}$$

3. Writing

$$\begin{aligned} \zeta &\equiv gx + fy + c, \\ cU &\equiv cS - \zeta^2 = Bx^2 - 2Hxy, \\ cV &\equiv cS_1 - \zeta^2 = (B + 3c\lambda_1)\, x^2 - 2\,(H - 3/2\, c\lambda_1^2)\, xy + c\lambda_1^3 y^2, \\ cW &\equiv cS_2 - \zeta^2 = (B + 3c\lambda_2)\, x^2 - 2\,(H - 3/2\, c\lambda_2^2)\, xy + c\lambda_2^3 y^2, \end{aligned} \tag{6}$$

it is easily verified that the three quadratic forms U, V, W are in involution, for the relevant condition

$$\begin{vmatrix} B & H & 0 \\ 3c\lambda_1 & -\frac{3}{2} c\lambda_1^2 & \lambda_1^3 \\ 3c\lambda_2 & -\frac{3}{2} c\lambda_2^2 & \lambda_2^3 \end{vmatrix} = 0 \tag{7}$$

is satisfied in virtue of (5).

U, V, W are therefore expressible in the form

$$\left.\begin{aligned} cU &\equiv l_1\xi^2 + m_1\eta^2 \\ cV &\equiv l_2\xi^2 + m_2\eta^2 \\ cW &\equiv l_3\xi^2 + m_3\eta^2 \end{aligned}\right\}, \tag{8}$$

where we can take

$$\xi \equiv x - \mu y, \ \eta \equiv x - \nu y, \tag{9}$$

where μ and ν are constants to be determined. To determine μ, ν we observe from (8) that $\xi\eta$ can differ only by a numerical multiplier from any of the three determinants

$$\frac{\partial\,(U, V)}{\partial\,(x, y)}, \ \frac{\partial\,(V, W)}{\partial\,(x, y)} \text{ and } \frac{\partial\,(W, U)}{\partial\,(x, y)}.$$

From this consideration, it will follow that the equation

$$(x - \mu y)(x - \nu y) = 0$$

is identical with $3cx^2 - 2Bxy + 2Hy^2 = 0$.

Hence,

$$\mu + \nu = \frac{2B}{3c}, \quad \mu\nu = \frac{2H}{3c}. \tag{10}$$

Substitution of (9) in (6) gives rise to the identities

$$\left.\begin{aligned} Bx^2 - 2Hxy &\equiv l_1(x - \mu y)^2 + m_1(x - \nu y)^2 \\ (B + 3c\lambda_1)x^2 - 2(H - \tfrac{3}{2}c\lambda_1^2)xy + c\lambda_1^3 y^2 &\equiv l_2(x - \mu y)^2 + m_2(x - \nu y)^2 \\ (B + 3c\lambda_2)x^2 - 2(H - \tfrac{3}{2}c\lambda_2^2)xy + c\lambda_2^3 y^2 &\equiv l_3(x - \mu y)^2 + m_3(x - \nu y)^2 \end{aligned}\right\}, \tag{11}$$

which are all *identically* satisfied if and only if

$$\left.\begin{aligned} l_1 &= K\nu^2, & m_1 &= -K\mu^2, \\ l_2 &= K(\nu + \lambda_1)^2, & m_2 &= -K(\mu + \lambda_1)^2, \\ l_3 &= K(\nu + \lambda_2)^2, & m_3 &= -K(\mu + \lambda_2)^2, \end{aligned}\right. \tag{12}$$

where

$$K = 3c/2(\nu - \mu). \tag{13}$$

We thus derive the following *canonical forms for a triad of cognate sextactic conics of a bicursal cubic :*

$$\left.\begin{aligned} S &\equiv K(\nu^2\xi^2 - \mu^2\eta^2) + \zeta^2 = 0 \\ S_1 &\equiv K[(\nu + \lambda_1)^2\xi^2 - (\mu + \lambda_1)^2\eta^2] + \zeta^2 = 0 \\ S_2 &\equiv K[(\nu + \lambda_2)^2\xi^2 - (\mu + \lambda_2)^2\eta^2] + \zeta^2 = 0. \end{aligned}\right\} \tag{14}$$

The triangle of reference is formed by the lines

$$\xi \equiv x - \mu y = 0, \ \eta \equiv x - \nu y = 0, \ \zeta \equiv gx + fy + c = 0,$$

and forms a common self-conjugate triangle to the three conics.

Hence, *the triad of cognate sextactic conics of a bicursal cubic, associated with a point of inflexion I_r, possesses a common self-conjugate triangle having I_r as a vertex and the associated harmonic polar L_r as the opposite side.**

Section II

Invariant Relation between Two Cognate Sextactic Conics

4. That two given conics S, S′ should each have six-pointic contact with a cubic obviously implies $2 \times (6 - 1) = 10$ conditions between the

* A more general result has been discussed in a different manner in my "Note on Conics of Double Osculation of a Cubic," to be published shortly in the *Proceedings of the National Academy of Sciences*, Allahabad.

coefficients of the cubic and the conics. Since the general cubic Γ involves 9 independent coefficients, it follows that *one* condition must be fulfilled between the coefficients of S and S′. We investigate this condition in the particular case when S, S′ are cognate sextactic conics of a cubic.

From §3, it follows that one of the three vertices, say C of the common self-conjugate triangle of S, S′ must be a point of inflexion of the required cubic Γ, and the opposite side AB must be the corresponding harmonic polar. If then, the equations of S, S′ referred to the triangle ABC be

$$\begin{aligned} S &\equiv l\xi^2 + m\eta^2 + n\zeta^2 = 0 \\ S' &\equiv l'\xi^2 + m'\eta^2 + n'\zeta^2 = 0, \end{aligned} \tag{15}$$

we must have by (12),

$$\frac{l}{n} = K\nu^2,\ \frac{m}{n} = -K\mu^2,\ \frac{l'}{n'} = K(\nu + \lambda_1)^2,\ \frac{m'}{n'} = -K(\mu + \lambda_1)^2,$$

where $K = \frac{3}{2}\cdot\frac{c}{\nu - \mu}$, (16)

and μ, ν are the roots of the quadratic

$$3t^2 + 2(\lambda_1 + \lambda_2)t + \lambda_1\lambda_2 = 0. \tag{17}$$

Eliminating λ_2 from the equations

$$\mu + \nu = -\tfrac{2}{3}(\lambda_1 + \lambda_2),\ \mu\nu = \tfrac{1}{3}\lambda_1\lambda_2,$$

we have

$$2 + 3\left(\frac{\mu}{\lambda_1} + \frac{\nu}{\lambda_1}\right) + 6\frac{\mu}{\lambda_1}\cdot\frac{\nu}{\lambda_1} = 0. \tag{18}$$

The three values of ϵ for which the conic $\epsilon S + S' = 0$, where S, S′ are defined by (15), breaks up into straight lines are the three quantities α, β, γ defined by

$$\alpha = -\frac{l'}{l},\ \beta = -\frac{m'}{m},\ \gamma = -\frac{n'}{n}.$$

By (16),

$$\frac{\alpha}{\gamma} = \left(\frac{\nu + \lambda_1}{\nu}\right)^2,\ \frac{\beta}{\gamma} = \left(\frac{\mu + \lambda_1}{\mu}\right)^2,$$

i.e.,

$$\frac{\lambda_1}{\nu} = \frac{\sqrt{\alpha} - \sqrt{\gamma}}{\sqrt{\gamma}},\ \frac{\lambda_1}{\mu} = \frac{\sqrt{\beta} - \sqrt{\gamma}}{\sqrt{\gamma}}. \tag{19}$$

Hence (18) gives after simplification

$$2\gamma + \sqrt{\gamma}(\sqrt{\alpha} + \sqrt{\beta}) + 2\sqrt{\alpha\beta} = 0. \tag{20}$$

But the three values α, β, γ are the three roots of the cubic

$$\Delta\epsilon^3 + \Theta\epsilon^2 + \Theta'\epsilon + \Delta' = 0, \tag{21}$$

where Δ, Θ, Θ', Δ' are the invariants of the pair of conics S and S′. Hence the condition that S, S′ should be cognate sextactic conics of a possible cubic reduces to the condition that the roots α, β, γ of (21) conform to the relation (20).

5. Suppose the roots α, β, γ of any cubic

$$at^3 + bt^2 + ct + d = 0 \tag{22}$$

satisfy the relation (20), which, when rationalized, gives

$$\{4\gamma^2 - (\beta\gamma + \gamma\alpha - 4\alpha\beta)\}^2 = 36\alpha\beta\gamma^2.$$

Hence

$$\left\{4\gamma^3 - \left(\frac{c}{a} + \frac{5d}{a\gamma}\right)^2\right\} = -36\frac{d\gamma}{a},$$

which, taken with

$$a\gamma^3 + b\gamma^2 + c\gamma + d = 0 \tag{23}$$

reduces to

$$(4b\gamma^2 + 5c\gamma + 9d)^2 = 36d(b\gamma^2 + c\gamma + d),$$

i.e.,
$$16b^2\gamma^4 + 40bc\gamma^3 + (25c^2 + 36bd)\gamma^2 + 54cd\gamma + 45d^2 = 0 \tag{24}$$

Dialytic elimination of γ from (23) and (24) gives the required condition that the roots of (22) satisfy (20). Taking the values of a, b, c, d corresponding to (21), we obtain the condition we have been seeking for, in the form

$$\begin{vmatrix}
\Delta & \Theta & \Theta' & \Delta' & 0 & 0 & 0 \\
0 & \Delta & \Theta & \Theta' & \Delta' & 0 & 0 \\
0 & 0 & \Delta & \Theta & \Theta' & \Delta' & 0 \\
0 & 0 & 0 & \Delta & \Theta & \Theta' & \Delta' \\
16\Theta^2, & 40\Theta\Theta', & 25\Theta'^2 + 36\Theta\Delta', & 54\Theta'\Delta', & 45\Delta'^2, & 0 & 0 \\
0, & 16\Theta^2, & 40\Theta\Theta', & 25\Theta'^2 + 36\Theta\Delta', & 54\Theta'\Delta', & 45\Delta'^2, & 0 \\
0, & 0, & 16\Theta^2, & 40\Theta\Theta', & 25\Theta'^2 + 36\Theta\Delta', & 54\Theta'\Delta', & 45\Delta'^2
\end{vmatrix} = 0 \tag{25}$$

Recognizing that (25) is a homogeneous function of the invariants of S and S′, it follows that the condition (25) remains unaltered for any transformation of the triangle of reference, and hence represents the *necessary* condition that two given conics S and S′ should be cognate sextactic conics of a possible cubic. The sufficiency or otherwise of this condition remains an *open* question.

CHEMOTHERAPY OF TUBERCULOSIS

Part I. Synthesis of Possible Lipophilic Chemotherapeuticals of the Sulphonamide and Sulphone Series derived from Fatty Acids, including those of the Chaulmoogra Group

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The present state of our knowledge in the Chemotherapy of Tuberculosis, the significance of the results of testing the drugs *in vitro* and *in vivo*, and the peculiar pathological features of the disease have been described by us recently.[1] In accordance with the ideas, work has been undertaken to synthesise compounds that are likely to act powerfully on the tubercle bacilli both *in vitro* and *in vivo*.

For the discovery of drugs lethal to the tubercle bacilli, there are three methods that could be followed:—

(1) to start from a compound showing action on the tubercle bacilli and by introducing substituents attempt to arrive at a more powerful drug; (2) to examine a cross-section of compounds belonging to diverse groups and structures to detect the structural features associated with tuberculocidal activity and (3) to design inhibitors that could effectively interfere with any of the vital nutritional, metabolic or respiratory processes of the bacilli so as to cause death; these inhibitors could be designed only on the basis of the knowledge of the chemistry of the abovementioned processes. We have undertaken work employing all these methods and the compounds synthesised are presented in this and the succeeding communications. The testing of the compounds is under way.

Of the numerous compounds and substances tested so far for their curative action in experimental tuberculosis, only derivatives of sulfanilamide and 4:4′-diaminodiphenyl sulphone as well as the antibiotic streptomycin, have shown very significant protective action. But these compounds have not shown the same degree of protection in tuberculosis and leprosy clinically. The synthesis and study of lipophilic derivatives of sulphanilamide and 4:4′-diaminodiphenyl sulphone were undertaken to try out whether this would lead to any compound or compounds with better protective action.

The present communication is concerned with the synthesis of some simple *fatty* acyl derivatives of the sulfanilamides in clinical usage and 4:4′-disubstituted diphenyl sulphones. Among the fatty acids used in this exploratory study, hydnocarpic acid has been chosen as the representative

of the choulmoogra group. The twenty-three compounds now prepared are listed in Table I.

TABLE I

Serial No.	Name of the compound	Molecular Formula	M.P./°C.	Nitrogen percentage	
				Found	Required
1	N^4-Formyl-N^1-hydnocarpyl sulphanilamide	$C_{23}H_{34}O_4N_2S$	123–26	6·4	6·5
2	N^4-Acetyl-N^1-hydnocarpyl sulphanilamide	$C_{24}H_{36}O_4N_4S$	144–46	6·5	6·3
3	N^4-*n*-Butyryl-N^1-hydnocarpyl sulphanilamide	$C_{26}H_{40}O_4N_2S$	143–47	6·0	6·0
4	N^4-*n*-Caproyl-N^1-hydnocarpyl sulphanilamide	$C_{28}H_{44}O_4N_2S$	125–27	5·7	5·6
5	N^4:N^1-Dihydnocarpyl sulphanilamide	$C_{38}H_6\ O_4N_2S$	128–30	4·5	4·4
6	4-Nitro-4′-hydnocarpylamido-diphenyl sulphone	$C_{28}H_{36}O_5N_2S$	162–63	5·5	5·5
7	4:4′-Dihydnocarpylamido-diphenyl sulphone	$C_{44}H_{64}O_4N_2S$	132–34	3·9	3·9
8	4-Nitro-4′-formamidodiphenyl sulphone	$C_{13}H_{10}O_5N_2S$	229–30 lit.[5], 234–35	8·5	9·0
9	4-Nitro-4′-butyramido-diphenyl sulphone	$C_{16}H_{16}O_5N_2S$	179–80	7·6	8·4
10	4-Nitro-4′-*n*-valeramidodiphenyl sulphone	$C_{17}H_{18}O_5N_2S$	170–71 sintg. at 158	7·5	7·7
11	4-Nitro-4′-*n*-capramidodiphenyl sulphone	$C_{18}H_{20}O_5N_2S$	159–60	7·2	7·4
12	4-Nitro-4′-*n*-heptamidodiphenyl sulphone	$C_{19}H_{22}O_5N_2S$	161–63	7·0	7·2
13	4:4′-Di-*n*-butyramidodiphenyl sulphone	$C_{20}H_{24}O_4N_2S$	229–30	7·1	7·2
14	4:4′-Di-*n*-valeramidodiphenyl sulphone	$C_{22}H_{28}O_4N_2S$	207–08	6·6	6·7
15	4:4′-Di-*n*-capramidodiphenyl sulphone	$C_{24}H_{32}O_4N_2S$	186–87	6·3	6·3
16	4:4′-Di-*n*-heptamidodiphenyl sulphone	$C_{26}H_{36}O_4N_2S$	166–67	6·3	5·9
17	4:4′-*bis*-Chloroacetamido-diphenyl sulphone	$C_{16}H_{14}O_4N_2SCl_2$	191–92	6·5	7·0
18	4:4′-*bis*-Glycolylamidodiphenyl sulphone	$C_{16}H_{16}O_6N_2S$	245–55 softg. at 230	7·5	7·7
19	4:4′-*bis*-Adipylamidodiphenyl sulphone	$C_{24}H_{28}O_6N_2S$	131–33	6·0	5·6
20	4:4′-*bis*-Sebacylamidodiphenyl sulphone	$C_{32}H_2O_3N_2S$	141–43	4·3	4·5
21	2-(*p*-*n*) Caproylaminobenzene-sulphonamido)-pyrimidine	$C_{16}H_{20}O_3N_4S$	213–15	16·2	16·1
22	2-(*p*-*n*-Caproylaminobenzene-sulphonamido)-4-methylpyrimidine	$C_{17}H_{22}O_3N_4S$	165–68	15·7	15·5
23	2-(*p*-*n*-Caproylaminobenzene-sulphonamido)-4:6-dimethyl pyrimidine	$C_{18}H_{26}O_3N_4S$	202–03	14·8	14·9

Of the synthetical aliphatic diacyl derivative of 4 : 4'-diaminodiphenyl sulphone (Nos. 13–16), some of the lower members were investigated by Nitti, Bovet and Hamon[2] for their antibacterial action, but others do not appear to have been reported in the regular literature so far.

Experimental

Hydnocarpic and Chaulmoogric Acids.—The two acids were prepared from *H. Wightiana* oil by an adaptation of the methods of Cole and Cardosa[3] as follows:—

A mixture of *H. Wightiana* oil (700 c.c.), absolute alcohol (700 c.c.) and con. sulphuric acid (100 c.c.) was heated under reflux for 8 hours. It was cooled and freed from excess of alcohol, sulphuric acid, and glycerol by repeated washing with water. On filtration a clear brown liquid, with a faint fruity odour was obtained; yield, 775 c.c. which contained a mixture of esters.

The esters prepared from a number of batches (4 l.), after dehydration by heating under reduced pressure, were then fractionated. The fraction boiling between 180–230°/10–12 mm., containing most of the ethyl esters of chaulmoogric and hydnocarpic acids, was collected. A broad initial separation of the two esters was effected by subjecting the above fraction to redistillation in a 2 l. Claissen flask with a six-inch Vigreax column. Two main fractions (1) b.p. 190–205°/10–12 mm. and (2) b.p. 210–25°/10–12 mm. were thus collected; these on further fractionation separately, furnished two fairly constant boiling fractions of colourless liquid of b.p. 195–98°/11 mm. and b.p. 216–20°/11 mm., the yield of the two fractions being 1800 c.c. and 1200 c.c. respectively.

The lower boiling fraction (270 c.c.), alcohol (600 c.c.), and potassium hydroxide (65 g.) in water (65 c.c.) were gently refluxed for one hour, cooled and acidified with dilute sulphuric acid. The solid obtained was filtered, pressed well free from the adhering oily product, washed carefully with small amounts of cold 60 per cent. alcohol and crystallised five times from 80 per cent. alcohol. Pure hydnocarpic acid was thus obtained, m.p. 59–60°; yield, 35 g.

On saponifying the higher boiling ester (270 c.c.) and working up as described above, pure chaulmoogric acid, m.p. 67–68°; was obtained; yield, 82 g.

Pure hydnocarpic acid, unlike its ethyl ester, does not keep well (*cf.* Van Nagelli and Vogt-Markins[4]) and so was used up as early as possible for further operations.

N^4-acyl-N^1-hydnocarpyl sulphanilamides (Nos. 1–4),—were synthesised by the action of (1·12) molecular proportion of hydnocarpyl chloride on the appropriate N^4-acyl sulphanilamides in pyridine solution.

N^4, N^1-Dihydnocarpyl sulphanilamide (No. 5),—was obtained by the action of slightly more than two molar proportions of hydnocarpyl chloride on sulphanilamide in pyridine solution.

4-Nitro-4′-hydnocarpylamidodiphenyl sulphone (No. 6) and *4 : 4′-Dihydnocarpylamidodiphenyl sulphone* (No. 7),—were obtained by the action of a slight excess of hydnocarpyl chloride on 4-nitro-4′-aminodiphenyl sulphone and 4 : 4′-diaminodiphenyl sulphone respectively in pyridine solution.

4-Nitro-4′-formamidodiphenyl sulphone (No. 8),—was prepared essentially by the procedure of Heyman and Heidelberger.[5]

The other normal fatty acyl derivatives of 4-nitro-4′-aminodiphenyl sulphone (Nos. 9–12) and of 4 : 4′-diaminodiphenyl sulphone (Nos. 13–16) were easily obtained by the action of slightly more than the calculated amount of the requisite acid chloride on 4-nitro-4′-aminodiphenyl sulphone and 4 : 4′-diamino-diphenyl sulphone respectively in pyridine medium.

4 : 4′-bis-Chloroacetamidodiphenyl sulphone (No. 17),—was obtained in fair yields by the action of a slight excess of chloro-acetyl chloride on diaminodiphenyl sulphone suspended in cold water in the presence of sodium acetate or bicarbonate.

4 : 4′-bis-Glycolamidodiphenyl sulphone (No. 18),—resulted in almost quantitative yields by boiling *bis*-4 : 4′-chloroacetamido diphenyl sulphonte with 20 parts of sodium acetate solution for 12 hours.

The n-*caproyl derivatives of sulphadiazine* (No. 21), *sulphamerazine* (No. 22), and *sulphamethazine* (No. 23),—were obtained in excellent yields by reacting excess of *n*-caproyl chloride with the respective sulphanilamides in pyridine. These were initially purified by reprecipitation with excess of dilute hydrochloric acid from cold aqueous solutions of their sodium salts.

Of the caproyl derivatives prepared, caproyl sulphadiazine has recently been reported by Finkelstein[6] also. The yields of the aforementioned compounds were uniformly good, and ranged from 80–90% for the recrystallised samples.

4 : 4′-bis-Adipylamidodiphenyl sulphone (No. 19),—4 : 4′-Diaminodiphenyl sulphone (25 g.) and adipic acid (14·6 g.; 2 mols.) in a 100 c.c. long necked round bottom flask, were heated together in an oil-bath first at 130–50° for one hour, and later at 150–70° for 4 hours. The melt was cooled, purified

through a dilute alkaline solution (charcoal), and fractionally crystallised from alcohol or acetone, yield 6 g.

Although the corresponding diethyl ester of the above amide, *viz.*, 4:4′-*bis*-*o*-carboethoxyvaleraminodiphenyl sulphone, has been synthesised by Gray and Platt[7] by the action of *o*-carbethoxy valeryl chloride on 4:4′-diaminodiphenyl sulphone, these authors have converted their esters directly to the disodium salt of 4:4′-*bis*-adipylamidodiphenyl sulphone.

4:4′-*bis*-*Sebacylamidodiphenyl sulphone* (No. 20),—was obtained by fusion of diaminodiphenyl sulphone (9·3 g.) with sebacic acid (15·2 g.; 2 mols.) first at 130–50° for one hour, and then at 150–70° for four hours. The reaction product was purified through dilute alkali and then crystallised from alcohol, yield 9 g.

We express our grateful thanks to Major-General Sir Sahib Singh Sokhey, Director, Haffkine Institute, Bombay, for his kind interest in these investigations. We are also thankful to Mr. M. H. Shah, B.Sc., for carrying out all the analysis.

Summary

Twenty-three compounds have been synthesised as possible lipophilic chemotherapeuticals of the sulphonamide and sulphone series. Among such compounds are the hydnocarpic acid derivatives of N^4-*n*-fatty acyl sulphanilamides, N^4, N^1-dihydnocarpylsulphanilamide, normal fatty-acyl derivatives of 4-nitro-4′-amino- and 4:4′-diamino-diphenylsulphones, 4:4′-*bis*-adipylamido- and 4:4′-*bis*-sebacylamido-diphenylsulphones, and the N^4-*n*-caproyl derivatives of 2-sulphanilamidopyrimidine, 2-sulphanilamido-4-methyl- and 2-sulphanilamido-4:6-dimethyl pyrimidines.

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CHEMOTHERAPY OF TUBERCULOSIS

Part II. Synthesis of N^4-Acyl-5-Alkylsulphathiazolones and 5: 5′-Alkylene *bis*-N^4-Acyl Sulphathiazolones

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Although it is eight years since Moore and Miller[1] first reported the synthesis of nine 5-alkyl sulphathiazolones and the promising chemotherapeutic activities exhibited by some of them in experimental bacterial infections, sulphathiazolones do not appear to have attracted attention from other workers in the field of chemotherapy. The one possible exception is sulphaethyl thiazolone which received passing notice from Cooper, Gross and Lewis[2] who found it to possess approximately the same antipneumococcal activity as sulphapyridine or sulphathiazole, an antistreptococcal action to that of sulphathiazole and antistaphylococcal activity of the same order as that of sulphathiazole or sulphadiazine. Cooper, *et al.*[2] were also of the opinion that whereas sulphaethyl thiazolone may perhaps cause fatal anæmia it was free from the serious defect in sulphadiazine of producing serious *urolithiasis* medicamenta in mice and rats. In the preliminary chemotherapeutic tests conducted, Moore and Miller[1] reported promising antistreptococcal activities for the 5-propyl-, 5-butyl-, 5: 5′-diethyl-sulphathiazolones and for the N^4-hexanoyl and heptanoyl derivatives of 5-butyl sulphathiazolone. Favourable antipneumococcal action was shown by 5-butyl, 5: 5′-dimethyl-, 5: 5′-diethyl-, and the N^4-hexanoyl substituted 5-butyl derivatives of sulphathiazolone, while 5-ethyl- and 5: 5′-diethyl sulphathiazolone were antistaphylococcal. Sulphaethyl thiazolone was absorbed as rapidly and its maximum concentration was higher on two dose levels than for sulfanilamide, sulphapyridine or sulphathiazole.

We were particularly interested in exploring the group of sulphathiazolones, carrying lipophilic alkyl radicals in the 5-position, for the treatment of tuberculosis and leprosy. Particular attention was paid to the synthesis of N^4-acylic compounds which were expected to be even more lipophilic than the free sulpha-alkylthiazolones. The inability in the early experiments to duplicate the higher yields reported by Moore and Miller[1] in the synthesis of the free 5-substituted sulphathiazolones by the acid hydrolysis of the corresponding N^4-acetyl derivatives, was also responsible for the election to synthesise exclusively N^4-acyl sulphathiazolones.

The 5-alkyl N^4-acyl sulphathiazolones and 5: 5′-alkylene-*bis*-N^4-acyl sulphathiazolones synthesised and which have not been reported hitherto, are tabulated. The N^4-acyl sulphathiazolones were prepared by the reaction of the appropriate acylsuphanilyl chloride with the requisite 2-amino-4-thiazolone in pyridine solution.

Substituted Sulphanilamidothiazolones

Serial No.	Name of the Compound	Molecular Formula	M.P./°C.	Nitrogen percentage	
				Found	Required
24	2:N^4-*n*-Butyryl sulphanilamidothiazolone	$C_{13}H_{15}O_4N_3S_2$	248–250	12·5	12·3
25	2-N^4-*n*-Valeryl sulphanilamidothiazolone	$C_{14}H_{17}O_4N_3S_2$	215–217	11·7	11·9
26	2-N^4-*n*-Caproyl sulphanilamidothiazolone	$C_{15}H_{19}O_4N_3S_2$	137–38	11·2	11·4
27	2-N^4-*n* Butyryl sulphanilamido-5-methylthiazolone	$C_{14}H_{17}O_4N_3S_2$	144–45	12·1	11·9
28	2-N^4-*n*-Valeryl sulphanilamido-5-methylthiazolone	$C_{15}H_{19}O_4N_3S_2$	135–36	11·0	11·4
29	2-N^4-*n*-Caproyl sulphanilamido-5-methylthiazolone	$C_{16}H_{21}O_4N_3S_2$	126–27	10·7	10·9
30	2-N^4-Acetyl-sulphanilamido-5-methylthiazolone	$C_{13}H_{15}O_4N_3S_2$	120–21	12·0	12·3
31	2-Sulphanilamido-5-ethylthiazolone	$C_{11}H_{13}O_3N_3S_2$	147–48	14·1	14·1
32	2-N^4-*n*-Butyryl sulphanilamido-5-ethylthiazolone	$C_{15}H_{19}O_4N_3S_2$	154–55	12·0	11·4
*33	2-N^4-*n*-Caproyl sulphanilamido-5-ethylthiazolone	$C_{17}H_2O_4N_3S_2$	178–72 Lit.,[1] 140–41	11·0	11·0
34	2-N^4-*n*-Butyryl sulphanilamido-5-*iso*-propylthiazolone	$C_{16}H_{21}O_4N_3S_2$	173–74	11·7	11·4
35	2-N^4-*n*-Caproyl sulphanilamido-5-*iso*-propylthiazolone	$C_{18}H_{25}O_4N_3S_2$	227–28	10·5	10·2
36	2-N^4-*n*-Butyryl sulphanilamido-5-*n*-hexylthiazolone	$C_{19}H_{27}O_4N_3S_2$	156–57	10·1	9·9
37	2-N^4-*n*-Valeryl sulphanilamido-5-*n*-hexylthiazolone	$C_{20}H_{29}O_4N_3S_2$	166–67	9·7	9·6
38	2-N^4-*n*-Butyryl sulphanilamido-5-phenylthiazolone	$C_{19}H_{19}O_4N_3S_2$	140–45	9·8	10·1
39	2-N^4-*n*-Valeryl sulphanilamido-5-phenylthiazolone	$C_{20}H_{21}O_4N_3S_2$	150–55	9·8	9·7
40	2-N^4-*n*-Caproyl sulphanilamido-5-phenylthiazolone	$C_{21}H_{22}O_4N_3S_2$	96–97 softg. at 70	9·4	9·9
41	5:5′-Diethylene-2:2′-*bis*-N^4-*n*-butyryl-sulphanilamidothiazolone	$C_{28}H_{32}O_8N_6S_4$	200–10 softg. at 180	11·4	11·8
42	5:5′-Hexamethylene-2:2′-*bis*-N^4-*n*-butyryl sulphanilamidothiazolone	$C_{32}H_{40}O_8N_6S_4$	125–45	10·9	11·0
43	5:5′-Hexamethylene-2:2-*bis*-N^4-*n*-valeryl sulphanilamidothiazolone	$C_{34}H_{44}O_8N_6S_4$	170–76 softg. at 155	11·0	10·6
44	5:5′Hexamethylene-2:2′-*bis*-N^4-*n*-caproyl sulphanilamidothiazolone	$C_{36}H_{48}O_8N_6S_4$	162–65	9·9	10·2

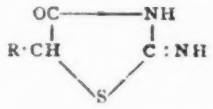
* This compound though differing in melting point from that of Moore and Miller (*loc. cit.*), gives correct analytical figure and exhibits marked activity in experimental streptococcal pneumococcal and *P. pestis* infections of white mice.[3]

Experimental

Pseudothiohydantoins.—The general procedure used for the synthesis of the 5-alkyl pseudothiohydantoins are exemplified in the preparation of 5-*iso*propyl-2-amino-4-thiazolone (No. 1). The 5: 5′-alkylenedipseudothiohydantoins (Nos. 5 and 6) were also prepared by a similar method, wherein the only modification adopted consisted in the use of the double the quantities of thionyl chloride, bromine and thiourea for each mole of the requisite dibasic acids.

5-iso*Propyl-2-amino-4-thiazolone.*—Isovaleric acid (55 c.c., 1 mol.) contained in a three-necked flask (750 c.c.) fitted with a reflux condenser, a dropping funnel and two calcium chloride guard tubes, was treated dropwise with thionyl chloride (50 c.c., 1·25 mols.). The reaction mixture was then heated on the water-bath for one hour when the evolution of the hydrochloric acid gas practically ceased. Bromine (27 c.c., 1 mol.), dried over concentrated sulphuric acid, was then added drop by drop to the hot reaction mixture. Heating on the boiling water-bath was continued for one hour after addition of all the bromine. The mixture was then cooled and cautiously treated with excess of alcohol (200 c.c.). The resulting solution of ethyl-α-bromo isovalerate was treated at room temperature with powdered thiourea (30 g., 1 mol.) and cautiously heated till the exothermic reaction set in. The reaction was moderated at this stage, by cooling if necessary, and completed by final refluxing for a further half an hour. The mixture was then diluted with excess of water, filtered and the aqueous acid solution of the hydrobromide basified with excess of ammonia. The resulting 5-*iso*propyl-2-aminothiazolone was crystallised from alcohol.

New pseudothiohydantoins synthesised now and numbered are set forth in Table II; pseudothiohydantoins not numbered are already known but prepared according to the procedure outlined above.



In the case of compounds Nos. 3 and 4, which were only feebly basic, the final purification through a dilute acid solution could not be adopted.

Compounds Nos. 1–4, crystallised from alcohol in colourless needles. Compounds Nos. 5 and 6 separated in colourless needles from alcohol, in which they were very sparingly soluble; these were advantageously purified by solution in dilute hydrochloric acid (charcoal) and reprecipitating by means

5-Substituted 2-amino-4-thiazolones

No.	Substituent (R) in position 5	Molecular Formula	M.P./°C.	Yield %	Nitrogen	
					Found	Required
	Methyl ..	..	..	67	..	..
	Ethyl ..	..	..	55	..	..
1	Isopropyl ..	$C_6H_{10}ON_2S$	224–25	35	18·0	17·7
	n-Butyl ..	..	..	75	..	..
2	*n*-Hexyl ..	$C_9H_{16}ON_2S$	187–89	68	14·2	14·0
3	*n*-Tetradecyl ..	$C_{19}H_{32}ON_2S$	167–72	60	8·9	9·0
4	Phenyl ..	$C_9H_8ON_2S$	228–29	84	14·8	14·5
5	Ethylene-5-pseudothiohydantoin	$C_8H_{10}O_2N_4S_2$	270 (dec.)	78	21·8	21·7
6	Hexamethylene-5-pseudothiohydantoin	$C_{12}H_{18}O_2N_4S_2$	249–51 (dec.)	72	17·5	17·8

of dilute ammonia in presence of appreciable amounts of alcohol when they separated as white needles and were analytically pure.

All the above substituted pseudothiohydantoins are soluble to varying extents in cold dilute sodium hydroxide from which they are regenerated with little change by dilute acetic acid.

The 5-alkyl-N^4-acyl sulphathiazolones (Nos. 24–30, 32–40) and the 5:5′-alkylene-*bis*-N^4-acylsulphathiazolones (Nos. 41–44) resulted by the action of 1·1 and 2·2 molecular proportions respectively of the requisite acylsulphanilyl chlorides on the suitable aminothiazolones in pyridine. The crude condensation products, obtained by dilution of the reaction mixtures with a large excess of water, were filtered, washed with water, and freed from traces of contaminating unreacted pseudothiohydantoins by thorough washing with dilute hydrochloric acid followed by water.

The final N^4-acyl sulphathiazolones were soluble in dilute ammonium hydroxide, the only exceptions being the 5-phenyl derivatives (Nos. 38–40). These were reprecipitated without change by dilute mineral acids. Occasionally, where the purity of the final product was in doubt, it was found to be advantageous to utilise the properties of the sulphathiazolones, *viz.*, dissolving in dilute ammonia. It was then possible to obtain pure samples by acidification of an ammonical solution (charcoal) of the acyl sulphathiazolones.

The yields of the purified acyl sulphathiazoles ranged between 30-40 per cent. of theory.

We express our grateful thanks to Major-General Sir Sahib Singh Sokhey, Director, Haffkine Institute, Bombay, and Dr. K. Ganapathi, D.Sc., for their kind interest in these investigations. We are also thankful to Mr. M. H. Shah, B.Sc., for carrying out all the analysis.

Summary

An attempt has been made to explore the little investigated but chemically and biologically interesting group of 2-sulphanilamidothiazolones, mostly carrying lipophilic alkyl radicals in the 5-position, for members likely to prove useful in the treatment of tuberculosis and leprosy. In the synthesis of the candidate compounds, emphasis has been laid on the N^4-*n*-fatty acyl derivatives of 2-sulphanilamido-5-substituted thiazolones in the expectation that these would be even more lipophilic than the free sulphanilamidothiazolones themselves.

A preparative method for the intermediate 2-amino-5-substituted thiazolones, starting with the corresponding mono- and dibasic fatty acids, has been worked out. New 5-substituted pseudothiohydantoins, derived from monobasic acids, are 5-*iso* propyl-, 5-*n*-hexyl-, 5-*n*-tetradecyl-, and 5-phenyl-2-amino-thiazolones. Among new 5: 5′-alkylene-*bis*-pseudothiohydantoins are 5: 5′-ethylene-*bis*-2: 2′-aminothiazolone and 5: 5′-hexamethylene-*bis*-2: 2′-aminothiazolone, prepared from adipic and sebacic acids respectively.

The following sulphonamidothiazolones have been synthesised: N^4-*n*-butyryl-, N^4-*n*-valeryl-, and the N^4-*n*-caproyl sulphanilyl derivatives of 2-amino-, 2-amino-5-methyl-, 2-amino-5-ethyl-, 2-amino-5-*iso*propyl-, 2-amino-5-*n*-hexyl-, and 2-amino-5-phenyl-thiazolones; and *bis*-N^4-*n*-butyryl, *bis*-N^4-*n*-valeryl- and *bis*-N^4-*n*-caproyl-sulphanilyl derivatives of 5: 5′-ethylene-*bis*-2-amino and 5: 5′-hexamethylene-*bis*-2-aminothiazolones.

2-Sulphanilamido-5-ethylthiazolone, prepared in the course of this study, differs in its physical characteristics from that of sulphaethylthiazolone as reported by the earlier workers. However, the present sample affords good analytical values and is markedly active in some acute bacterial infections.

References

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXVIII. Synthesis of 6-Hydroxy Primetin

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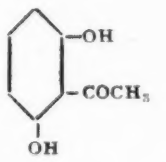
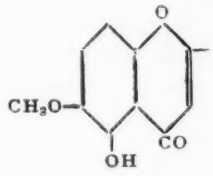
Since it has now been definitely established that gardenin is a flavonol having the rare 5:6:8- arrangement of hydroxyls in the condensed benzene ring,[1] analogous flavones could also be expected to be discovered in nature. For their synthesis, a procedure similar to the one adopted for the total synthesis of 5:6:8-trihydroxy flavonol[1] (6-hydroxy galangin) could be followed. This would start from γ-resacetophenone (I) and pass through the 6-methoxy-5-hydroxy compounds (II),[2] but as it involves a large number of steps, it may be considered to be tedious and inconvenient.

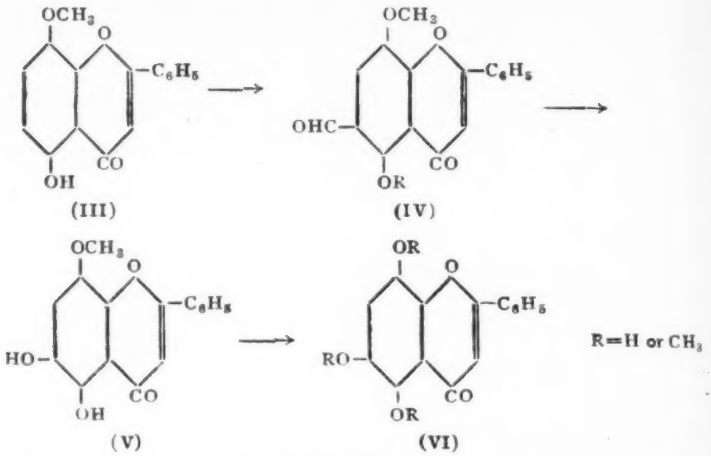


(I)

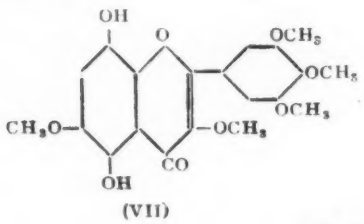


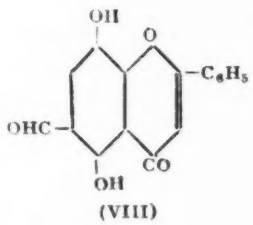
(II)

A new and more direct route involving the two stage process of nuclear oxidation[3] has now been explored and successfully worked out. It has been rendered possible by the simplified synthesis of primetin, described by Rajagopalan, Rao and Seshadri.[4] In this, primetin is partially methylated to 5-hydroxy-8-methoxy flavone (III). On being condensed with hexamine in glacial acetic acid solution, it yields the 6-aldehyde (IV) in 80% yield. That the 6-position is activated by the 5-hydroxyl in this reaction has been shown in a closely related case by Murti and Seshadri.[5] The above aldehyde (IV) is easily oxidised to 5:6-dihydroxy-8-methoxy flavone (V) by means of alkaline hydrogen peroxide. The colour reactions of this product are in agreement with the given structure. It is demethylated with hydriodic acid to 6-hydroxy primetin (VI, R = H) and also methylated to yield 5:6:8-trimethoxy flavone (VI, R = CH_3).



A shorter route for the synthesis of 6-hydroxy primetin seemed to be possible. In a test experiment, it was noticed that gardenin quinol (VII)[1] did not yield any product on treatment with hexamine. Hence it appeared that the 8-hydroxyl group does not activate the 7-position adequately. On the other hand, it had been established that the 6-position is activated by the 5-hydroxyl group quite satisfactorily. Therefore, if primetin itself could be condensed with hexamine, it would yield the 6-aldehyde (VIII), which could be directly oxidised to 6-hydroxy primetin. However, the reaction was not found to proceed well and the aldehyde was obtained in an impure condition and in a poor yield and hence the scheme had to be abandoned.





Experimental

5-Hydroxy-8-methoxy flavone (III).—This was first prepared by Nagai and Hattori[6] by methylation of primetin with diazomethane. Baker[7] obtained it by the partial demethylation of 5:8-dimethoxy flavone. The partial methylation of primetin has now been carried out very satisfactorily using dimethyl sulphate in dry acetone medium.

Primetin (1·0 g.) dissolved in acetone (100 c.c.) was treated with freshly distilled dimethyl sulphate (0·45 c.c.) and potassium carbonate (5·0 g.) and refluxed for 6 hours. The potassium salts were filtered off and washed with warm acetone. The solvent was distilled off and the residue treated with a small quantity of alcohol and filtered. The solid thus obtained when crystallised from alcohol, yielded 5-hydroxy-8-methoxy flavone as thin yellow needles melting at 210°. It gave an intense bluish green colour with alcoholic ferric chloride. Yield 0·7 g.

5-*Hydroxy*-8-*methoxyflavone*-6-*aldehyde* (*IV*).—The above compound (0·6 g.) in glacial acetic acid (20 c.c.) was heated with hexamine (2·0 g.) for 6 hours in a boiling water-bath. The hot solution was treated with hot hydrochloric acid (1 : 1, 20 c.c.), cooled and diluted with water. The yellow solid that separated was filtered and washed with water. Crystallisation from alcohol-acetic acid mixture yielded the aldehyde as very fine yellow needles melting at 246–47°. It gave a bluish green colour with alcoholic ferric chloride. It was sparingly soluble in ethyl acetate, alcohol, benzene and acetone. Yield 0·5 g. (Found: C, 68·7, H, 4·3; $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%).

The 2 : 4-dinitrophenyl hydrazone, prepared by refluxing an alcoholic solution of the aldehyde with dinitro-phenylhydrazine melted at 320° (decomp.).

5 : 6-*Dihydroxy*-8-*methoxy flavone* (*V*).—The above aldehyde (0·5 g.) was dissolved in pyridine (20 c.c.) and sodium hydroxide (2·1 c.c. of 1 N; 1·2 mole) was added. The solution was cooled in ice and treated with 6% hydrogen peroxide (3 c.c.), added drop by drop, with shaking. The flask was corked and left at room temperature for 2 hours. The solution was neutralised with ice-cold dilute hydrochloric acid. The solid obtained was filtered and crystallised from alcohol. 5 : 6-Dihydroxy-8-methoxy flavone separated as orange-yellow fine needles melting at 184–85°. With alcoholic ferric chloride, it gave a green colour which slowly changed to brown. It dissolved in aqueous sodium hydroxide to give a pale yellow solution. (Found: C, 67·4; H, 4·2; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

5 : 6 : 8-*Trihydroxy flavone* (6-*Hydroxy primetin*) (*VI*, $R = H$).—5 : 6-Dihydroxy-8-methoxy flavone (0·3 g.) was dissolved in acetic anhydride (5 c.c.) and treated with hydriodic acid (10 c.c., d. 1·7) with cooling. The solution was heated in an oil-bath at 140° for one hour. The resulting product was diluted with water saturated with sulphur dioxide, when a yellow solid separated out. This was filtered and crystallised from dilute alcohol, when it separated as pale yellow short needles melting at 236–37°.

With alcoholic ferric chloride, it gave a brown colour. The colour deepened considerably with further addition of the reagent. In aqueous sodium hydroxide it formed a deep red solution, rapidly changing to brown pink, which slowly faded to brownish yellow and finally yellow. It dissolved in aqueous sodium carbonate to give a deep violet-brown solution fading slowly to yellow. It was partially soluble in aqueous sodium bicarbonate to give a pale brown colour. (Found: C, 66·9; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

5:6:8-*Triacetoxy flavone*.—The trihydroxy flavone (0·1 g.) was dissolved in acetic anhydride (8 c.c.) and treated with a few drops of dry pyridine and refluxed for 2 hours in an oil-bath. The reaction product was poured into water containing pieces of ice. The colourless solid was filtered and crystallised from ethyl acetate. The triacetoxy flavone came out as thin rectangular plates melting at 214°. (Found: C, 63·7; H, 4·3; $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·0%).

5:6:8-*Trimethoxy flavone* (*VI*, $R = CH_3$).—5:6-Dihydroxy-8-methoxy flavone (V) (0·2 g) in acetone (50 c.c.) was refluxed with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (2·0 g.) for 20 hours. The potassium salts were filtered off and washed with warm acetone. On distilling off the solvent from the filtrate and adding water, a crystalline solid separated out. When crystallised from very dilute alcohol, the trimethoxy flavone separated as thin colourless plates melting at 158–59°. (Found: C, 69·0; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

Summary

For the synthesis of 5:6:8-trihydroxy flavone (6-hydroxy primetin), the two stage ortho-oxidation process is applied to primetin monomethyl ether. A good yield of the 6-aldehyde is obtained, which undergoes oxidation to 5:6-dihydroxy-8-methoxy flavone. Subsequent demethylation yields 6-hydroxy primetin. Its properties and reactions and derivatives are described.

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4. Rajagopalan, Rao and Seshadri .. *Ibid.*, 1947, **25**, 432.
5. Murti and Seshadri .. *Ibid.*, 1949, **29**, 221.
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ANALYSIS OF THE ABSORPTION BANDS OF THE URANYL SALTS

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1. Introduction

A remarkable characteristic of the fluorescence spectra of uranyl salts is that they are independent both in respect of the intensity distribution as well as of the frequencies of the individual members of the wavelength of the exciting radiation. The exciting frequency should be equal or higher than that of the common fluorescence and absorption band and the entire fluorescence spectrum is emitted. Whatever be the exciting radiation—visible or ultra-violet light, X-rays or cathode rays—the same spectrum is always obtained. In the overlapping region of the fluorescence and absorption spectra two close lying common bands (named a_0 and b_0 in absorption) are sometimes observed which at low temperatures show an interesting relationship in the two spectra. In fluorescence the lower frequency band b_0 is always more intense than the a_0 band while in absorption the reverse is usually the case. These significant facts led the present author (1945) to suggest that transitions to the ground levels in the uranyl ion is from a single upper state and that the origin of the b_0 and a_0 bands is due to transitions to this state from the two low lying electronic states (named X and Σ), the latter of these being the ground state. The fluorescence spectra of several uranyl salts at liquid air temperature were explained on the basis of this idea and the fluorescence bands were shown to be due to the transitions from the single upper state to the various vibrational levels of the ground states. The absorption spectra can also be interpreted in the same way by taking into account the vibrational levels associated with excited state. It is important to keep in view that at low temperatures, the vibrational levels of the ground state will ordinarily not take part in absorption as the population of molecules in all such levels as are above the ground state will itself be very small. Inspite of this factor there is still some probability of absorption taking place from these levels, the intensity of such bands depending upon the transition probability and the operation of the Franck-Condon principle. It is, however, obvious that the low population of

molecules which exponentially decreases with the energy separation will make it impossible for much higher levels to take part in absorption at low temperatures. Confirmation of these ideas is obtained from the fluorescence and absorption spectra. It is well known for example, that the fluorescence spectra extend towards the red side of common fluorescence and absorption bands (*e.g.*, a_0 and b_0). Even in these bands, on account of considerations of transition probability and Boltzmann distribution factor interesting intensity changes referred to already are observed. It is also noteworthy that with thick layers of the salt, the absorption spectra can be pushed towards the region of fluorescence much more at higher temperatures than at lower temperatures (Nichols and Howes, 1919).

In the interpretations suggested by Van Heel (1925) and M. Freymann, T. Guilmart and R. Freymann (1946) there has been no attempt made to recognise the facts mentioned above. Both the fluorescence and absorption bands are shown to involve vibrational levels extending upto a few thousand wave numbers above the excited and the ground states. In the analysis of the absorption bands of uranylacetate by the latter authors two bands at 20756 cm.$^{-1}$* and 20593 (a_0 and b_0 bands) have been respectively interpreted as (0, 0′) and (1, 1′) bands, *i.e.*, as the electronic band and as a band arising from the first vibrational level of the symmetric valence frequency ν_1 in the ground state to the first vibrational level of the same frequency in the upper state. As $\nu_1 = 860$ in the ground state and $\nu_1' = 720$ in the excited state and this accounts for the frequency separation of about 140 in the two bands. The analysis is obviously arbitrary because at low temperatures no strong absorption band can possibly arise from a level as high as 860 above the ground state and also because if a strong (1, 1′) band exists there is no reason why a (1, 0′) band at 19896 should be entirely absent.

2. Analysis of the Absorption Spectra

Uranyl acetate (*crystalline*)

For comparison with the analysis of Freymann and others, the values of absorption bands as given by these authors have been used. These values slightly differ from those of Nichols and Howes and we have therefore taken the separation between the two lower states (A–B interval) as 163 instead of 150 as taken earlier in the fluorescence spectra. The deformational frequency $\nu_2 = 235$ as before and the values of the symmetric valence frequency ν_1' in the excited state $= 725$ and $\nu_2' = 220$. In Table I the analysis of the absorption bands is displayed where in the last column the same due

* All frequencies are given in wave numbers.

to Freymann and others is also given. In the analysis given by these authors the anti-symmetric valence frequency ν_3 occurs only in the ground state and its value as adopted by them is 930.

TABLE I

Analysis of Uranyl Acetate (crystalline) spectrum

Designation	ν obs.	ν cal.	Our assignment	Assignment due to Freymann, etc.	Remarks
b ..	20593 624	20593	b_0	$a_0-\nu_1'-\nu_1$	
a ..	20756	20756	a_0	a_0	Group I
c ..	20824	20813	$b_0+\nu_2'$	$a_0+2\nu_1'-\nu_2-2\nu_2$	
f ..	20903	20976	$a_0+\nu_2'$	$a_0-2\nu_1'-\nu_1-\nu_2$	
g ..	21032	21033	$b_0+2\nu_2'$	$a_0-2\nu_1'-\nu_3-\nu_2$	
c ..	21250 300	21246	$a_0+\nu_1'-\nu_2$	$a_0+2\nu_1'-\nu_3$	
b ..	21329 365	21318	$b_0+\nu_1'$	$a_0+2\nu_1'-\nu_1$	
a ..	21493	21481	$a_0+\nu_1'$	$a_0+\nu_1'$	Group II
e ..	21584	21538	$b_0+\nu_1'+\nu_2'$	$a_0+3\nu_1'-\nu_3-2\nu_2$	
f ..	21657	21701	$a_0+\nu_1'+\nu_2'$	$a_0+3\nu_1'-\nu_1-2\nu_2$	
g ..	21744	21758	$b_0+\nu_1'+2\nu_2'$	$a_0+3\nu_1'-\nu-\nu_2$	
h ..	21944	21921	$a_0+\nu_1'+2\nu_2'$	$a_0+3\nu_1'-\nu_3$	
c ..	21975	21971	$a_0+2\nu_1'-\nu_2$	..	
b ..	026 22060	22043	$b_0+2\nu_1'$	$a_0+3\nu_1'-\nu_1$	
a ..	22207	22206	$a_0+2\nu_1'$	$a_0+2\nu_1'$	Group III
e ..	22304	22263	$b_0+2\nu_1'+\nu_2'$	$a_0+\nu_1'-\nu_3-2\nu_2$	
f ..	22444	22426	$a_0+2\nu_1'+\nu_2'$	..	
g ..	22505	22483	$b_0+2\nu_1'+2\nu_2'$	$a_0+4\nu_1'-\nu_3-\nu_2$	
h ..	22666	22646	$a_0+2\nu_1'+2\nu_2'$	..	
c ..	22702	22696	$a_0+3\nu_1'-\nu_2$	$a_0+4\nu_1'-\nu_3$	
b ..	22756 91	22768	$b_0+3\nu_1'$	$a_0+4\nu_1'-\nu_1$	
a ..	22944	22931	$a_0+3\nu_1'$	$a_0+3\nu_1'$	Group IV
e ..	23041	22988	$b_0+3\nu_1'+\nu_2'$	..	
f ..	23150	23751	$a_0+3\nu_1'+\nu_2'$	$a_0+6\nu_1'-2\nu_1-\nu_2$	
h ..	23362	23371	$a_0+3\nu_1'+2\nu_2'$	$a_0+6\nu_1'-2\nu_1$	
b ..	23521	23493	$b_0+4\nu_1'$	$a_0-5\nu_1'-\nu_1$	
a ..	23649	23656	$a_0+4\nu_1'$	$a_0-4\nu_1'$	Group V
f ..	23872	23876	$a_0+4\nu_1'+\nu_2'$	$a_0-7\nu_1'-2\nu_1-\nu_2$	
h ..	24091	24096	$a_0+4\nu_1'+2\nu_2'$	$a_0-7\nu_1'-2\nu_1$	
f ..	24588	24601	$a_0+5\nu_1'+\nu_2'$	$a_0+8\nu_1-2\nu_1-\nu_2$	Group VI
h ..	24795	24821	$a_0+5\nu_1'+2\nu_2'$	$a_0+8\nu_1'-2\nu_1$	

Uranyl Chloride

The wave number values of the absorption bands are given in an earlier paper. $\nu_1' = 725$ and $\nu_2' = 225$ and the other intervals are as before (*i.e.*, A–B $= 174$ and $\nu_2 = 246$).

TABLE II. *Analysis of Uranyl Chloride Spectrum*

Design	ν obs.	ν cal.	Assignment	Remarks
E ..	20270			Observed in fluorescence also
D ..	20338			
C (*c*) ..	20439	20463	$a_0-\nu_2$	
B (*b*) ..	20534	20535	b_0	
e ..	20760	20760	$b_0+\nu_2'$	Group I
c ..	21205	21188	$a_0+\nu_1'-\nu_2$	
b ..	21287	21260	$b_0+\nu_1'$	
a ..	21402	21434	$a_0+\nu_1'$	
e ..	21505	21485	$b_0+\nu_1'+\nu_2'$	Group II
f ..	21546?	21659	$a_0+\nu_1'+\nu_2'$	
g ..	21716	21710	$b_0+\nu_1'+2\nu_2'$	
h ..	21855	21884	$a_0+\nu_1'+2\nu_2'$	
c ..	21905	21913	$a_0+2\nu_1'-\nu_2$	
b ..	21985	21985	$b_0+2\nu_1'$	
a ..	22135	22159	$a_0+2\nu_1'$	Group III
e ..	22201	22210	$b_0+2\nu_1'+\nu_2'$	
f ..	22351	22384	$a_0+2\nu_1'+\nu_2'$	
c ..	22641	22638	$a_0+3\nu_1'-\nu_2$	
b ..	22733	22710	$b_0+3\nu_1'$	
f ..	23097	23109	$a_0+3\nu_1'+\nu_2'$	Group IV
g ..	23226	23160	$b_0+3\nu_1'+2\nu_2'$	
h ..	23328	23334	$a_0+3\nu_1'+2\nu_2'$	
c ..	23382	23363	$a_0+4\nu_1'-\nu_2$	Group V
f ..	23838	23834	$a_0+4\nu_1'+\nu_2'$	

Uranyl Sulphate

The $1/\lambda$ values are given by Nichols and Howes (see page 177 of their monograph). $\nu_1' = 683$, and $\nu_2' = 220$. The other intervals in the ground state are the same as before (*i.e.*, A–B = 165, $\nu_2 = 258$).

TABLE III. *Analysis of Uranyl Sulphate Spectrum*

Design	νobs.	νcal.	Assignment	Remarks
b ..	20354	20332	b_0	
a ..	20451	20494	a_0	
	94?			Group I
e ..	20561	20552	$b_0+\nu_2'$	
f ..	20686	20714	$a_0+\nu_2'$	
c ..	20928	20921	$a_0+\nu_1'-\nu_2$	
b ..	21018	21015	$b_0+\nu_1'$	
a ..	21151	21177	$a_0+\nu_1'$	Group II
e ..	21273	21235	$b_0+\nu_1'+\nu_1'$	
f ..	21397	21397	$a_0+\nu_1'+\nu_2$	
c ..	21595	21604	$a_0+2\nu_1'-\nu_2$	
b ..	21692	21698	$b_0+2\nu_1'$	Group III
a ..	21859	21860	$a_0+2\nu_2'$	
f ..	22084	22080	$a_0+2\nu_1'+\nu_2'$	
c ..	22287	22287	$a_0+3\nu_1'-\nu_2$	
b ..	22360	22381	$b_0+3\nu_1'$	
e ..	22596	22601	$b_0+3\nu_1'+\nu_2'$	Group IV

Uranyl Potassium Sulphate

The $1/\lambda$ values are given by Nichols and Howes (see page 178 of their monograph). $\nu_1' = 700$, $\nu_2' = 170$. Other intervals are the same as before (*i.e.*, A–B = 90 and $\nu_2 = 172$).

TABLE IV. *Analysis of Uranyl Potassium Sulphate Spectrum*

Design	ν obs.	ν cal.	Assignment	Remarks
b ..	20350) 96	20385	b_0	Group I
a ..	20479	20475	a_0	
c ..	..	20303	$a_0 - \nu_2$	
e ..	20568	20555	$b_0 + \nu_2'$	
f ..	20644	20645	$a_0 + \nu_2'$	
g ..	20719	20725	$b_0 + 2\nu_2'$	
h ..	20786	20815	$a_0 + 2\nu_2'$	
b ..	21068) 93	21085	$b_0 + \nu_1'$	Group II
a ..	21164	21175	$a_0 + \nu_1'$	
f ..	21364	21345	$a_0 + \nu_1' + \nu_2'$	
c ..	21740	21703	$a_0 + 2\nu_1' - \nu_2$	Group III
b ..	21794	21785	$b_0 + 2\nu_1'$	
a ..	21885	21875	$a_0 + 2\nu_1'$	
f ..	22046	22045	$a_0 + 2\nu_1' + \nu_2$	
c ..	22417	22403	$a_0 + 3\nu_1' - \nu_2$	Group IV
b ..	22482	22485	$b_0 + 3\nu_1'$	
a ..	22567	22575	$a_0 + 3\nu_1'$	
e ..	22663	22655	$b_0 + 3\nu_1' + \nu_2'$	
f ..	22769	22745	$a_0 + 3\nu_1' + \nu_2'$	
h ..	22894	22915	$a_0 + 3\nu_1' + 2\nu_2'$	
c ..	23121	23103	$a_0 + 4\nu_1' - \nu_2$	Group V
a ..	23237	23275	$a_0 + 4\nu_1'$	

Autunite

The measurements of wavelengths are given by Van Heel (1925). $\nu_1' = 700$ and $\nu_2' = 233$. The intervals in the ground state are the same as before (*i.e.*, A–B = 114, $\nu_2 = 218$).

TABLE V. *Analysis of Autunite Spectrum*

Int.	Design	ν obs.	ν cal.	Assignment	Remarks
S ..	*b*	19848	19848	b_0	Group I
– ..	*a*	..	19962	a_0	
W* ..	*g*	20327	20314	$b_0 + 2\nu_2'$	
S ..	*b*	20558	20548	$b_0 + \nu_1'$	Group II
W ..	*g*	21016	21014	$b_0 + \nu_1' + 2\nu_2'$	
S ..	*b*	21246	21248	$b_0 + 2\epsilon_1'$	Group III
M ..	*a*	21330	21362	$a_0 + 2\nu_1'$	
W ..	*g*	21684	21702	$b_0 + 2\nu_1' + 2\nu_2'$	
W ..	*c*	21869	21844	$a_0 + 3\nu_1' - \nu_2$	Group IV
W ..	*a*	22023	22062	$a_0 + 3\nu_1'$	
W ..	*b*	21950	21948	$b_0 + 3\nu_2'$	

* Weak.

Uranyl Fluoride II

The wavenumber values are given in an earlier paper. A–B interval $= 150$, $\nu_1' = 715$, $\nu_2' = 243$.

TABLE VI. *Analysis of Uranyl Fluoride II Spectrum*

Design	ν obs.	ν cal.	Assignment	Remarks
b ..	20082	20082	b_0	Group I
a ..	20234	20232	a_0	
f ..	20475	20475	$a_0+\nu_2'$	
b ..	20784	20797	$b_0+\nu_1'$	This band splits up into three Group II
a ..	20951	20947	$a_0+\nu_1'$	
f ..	21188	21190	$a_0+\nu_1'+\nu_2'$	
b ..	21507	21512	$b_0+2\nu_1'$	Group III
a ..	21682	21662	$a_0+2\nu_1'$	
f ..	21930	21905	$a_0+2\nu_1'+\nu_2'$	
b ..	22190	22227	$b+3\nu_1'$	Group IV
a ..	22418	22387	$a+3\nu_1'$	

3. General Remarks

The absorption spectra of six uranyl salts at liquid air temperature have been explained. Mostly, the two levels in the ground state which are separated by a small frequency interval of nearly 150 take part in absorption. The appearance of the series *c*, however, involves a level nearly 220 above the lowest state. This series corresponds to the C series in fluorescence for which the transition probability is higher. The '*f*' series involves the deformational frequency in the excited state. The intensity of these series is in general high. The necessity of using higher levels in the ground state does not arise. Similar remarks as made in connection with the discussion of fluorescence spectra also apply here. The slight displacement in the minima of potential energy curves is also in accordance with the maximum intensity of the absorption bands being in the second or the third group. The appreciable change in the symmetric valence frequency ν_1 from 860 to $\nu_1' = 700$ on excitation accounts for the comparatively longer ν_1 progression.

Some complicated phenomena are observed in the absorption spectra. The bands are usually sharp in the beginning but they get broader and more diffuse towards the ultra-violet. According to the ideas of molecular spectroscopy if higher members belonging to a series in which sharp bands also appear at the beginning of the series are diffuse, it is a sufficient proof of pre-dissociation. The weak continuous absorption which is superposed

on the discrete absorption in the spectra of uranyl salts is most probably due to scattering effect due to the powder form of the salt. It may not be interpreted as a repulsive state, specially because the intensity of the continuous absorption is found to increase with temperature and that this absorption is stronger towards the ultra-violet. The splitting observed in some bands (specially *b* bands) in the higher groups cannot be clearly understood. This splitting causes some change in the frequency intervals as the most intense component of the splitted band does not lie at the centre of gravity of the initial band.

4. Summary

The absorption spectra of several uranyl salts have been interpreted in a manner similar to that adopted for the fluorescence spectra. Most of the bands arise out of the two closely spaced levels except for one series which arises from about 220 above the ground state. In view of the high transition probability for this series, its existence is shown to be justified. The necessity of using much higher levels (as high as 2000 as done by earlier workers) does not arise.

I express my thanks to Sir C. V. Raman and also to Dr. R. K. Asundi for helpful discussion.

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THE INFLUENCE OF WEATHER CONDITIONS ON LONG DISTANCE SHORT WAVE TRANSMISSION*

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Abstract

The field strengths at Waltair, of signals radiated from Madras, Calcutta and Bombay stations of the All India Radio on the 41 and 49 metre bands, have been studied over a period of seven months. The measurements have been made between 7-30 hrs. to 9-00 hrs. Indian Standard Time daily. The day-to-day variations of the field strengths of the received signals are presented, month by month, in the form of graphs and discussed.

The study of these curves shows that:

1. During the wet season there is a definite relationship between the field strengths of the received signals and the percentage humidities in the atmosphere along the path of the wave—a rise or fall in humidity producing a corresponding fall or rise in the received signal strengths.

2. Further, these effects are more pronounced when the percentage humidities are around about 85%.

3. In cases where the humidities are much lower, there appears to be no relation between these two quantities.

This abnormal transmission, especially during wet season, is traced to reflection at low levels, produced by clouds or zones of condensation or by water vapour molecules themselves.

Introduction

The study was carried out mainly on the 41 metre band. The choice of the subject and the wave band was prompted by a peculiar type of rapid fading, details of which are already published by the authors (1949), observed in the summer months, chiefly on the 41 and the 61 metre bands, during the evening and night transmissions from All India Radio, Madras. As a preliminary to the above problem it was suggested that the field strengths of certain Indian Broadcasting stations specially on the 41 and the 61 metre bands could be measured over a considerable period of the year and their

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variations studied in relation to the meteorological conditions along the path of propagation of the wave. In recent years the propagation of radio waves through troposphere has received considerable attention but all work was confined to " above 30 Mc/s " and very little work seems to have been done below 30 Mc/s.

Earlier experiments by several observers, amongst whom may be mentioned Mitra (1936), Bajpai and Pant (1939), Nasilov (1938), Martyn, Munro, Bannon and Higgs, and Watson Watt, Wilkins and Bowen (1940) have shown how the meteorological conditions of the atmosphere affect the state of the Ionosphere and the propagation of the wave, and also cause certain allied phenomena.

Experiment

The apparatus used in the present investigation consists of a Hallicrafters communications receiver model S 40-A, used in conjunction with a calibrated S-meter to measure the field strengths of the received signals and a standardised aerial erected on the roof of the laboratory which is situated on the summit of a hill, thus making the measurements uninfluenced by the surroundings.

General Plan of Investigation

The variation of field strengths of signals radiated from the three A.I.R. stations, namely, Madras, Calcutta and Bombay, were studied. The positions of the three stations and their distances from Waltair and their operating wavelengths are given below:

Station	*Distance*	*Latitude*	*Longitude*	*Operating wavelength/Meters*
Waltair ..	..	17–44′N	82–83′E	..
Madras ..	640 km.	13–04′N	80–17′E	41·32
Calcutta ..	800 km.	22–34′N	83–24′E	41·61
				49·92
Bombay ..	1150 km.	18–55′N	72–54′E	41·44

The three stations are situated in three different directions with respect to Waltair and an attempt was made to see how far the conditions of the atmosphere as observed on the ground, affect the propagation of the wave along its ionospheric path from the radiating to the receiving end.

Observations were made from 7-30 hrs. to 9-00 hrs. Indian Standard Time (I.S.T.) on the programmes radiated from Madras, Calcutta and Bombay, at intervals of 10 minutes. The study extended over a period of 7 months. The mean of the values of the field strengths observed during

the 10 minutes intervals from 7-30 hrs. to 9-00 hrs. on a particular day, is taken as representing the field strength for the day. The daily mean values of the signal strengths and their variation from day to day are presented and discussed.

Results

The daily variations of field strengths are presented month by month, in the form of graphs plotted with the day of the month as the abscissa and the corresponding signal strength as the ordinate. The signal strengths are expressed in field strengths measured in decibels above 1 microvolt/metre input to the receiver.

December 1947

The daily mean field strengths of the received signals throughout the month of December 1947 are shown in Fig. 1. The figure is in three sections; the top section shows the daily mean values of field strengths at Waltair of signals radiated from A.I.R. Madras (41·32 m. 7,260 kc/s), the middle section refers to radiations from A.I.R. Calcutta (49·92 m. 6,010 kc/s) and the bottom section to those from Bombay (41·44 m. 7,240 kc/s).

A study of the continuous line curves shows that signals from the three stations show a marked fluctuation in intensity between the 13th and the 25th instants. The field strength at Waltair of the Calcutta and Bombay signals reach values less than 1 μv/m. about the 14th instant and continue at that value till the 25th. Later there is a slight rise by the 29th instant. In contrast to this, Madras signals, while showing a rise in intensity like the Calcutta signals and Bombay signals about the 13th show a rise in intensity on the 19th and again a fall to 1 μv/m. on the 23rd instant. From the 27th onwards the field strengths remain steady.

It should be interesting to see what factors are likely to contribute to this large variation in field strengths of the three stations during this period.

Weather during this period

From a study of the Daily Weather Reports, issued by the India Meteorological Department, it is found that the weather during the period under observation was mainly governed by three depressions, one on the 13th in the Bay of Bengal, a second on the 17th in the Arabian Sea and a third on the 20th in the Bay of Bengal and from the 13th to the 25th considerable rain fell over the country.

It would be interesting to see how far the presence of moisture in the atmosphere is related to the attenuation of the signals from the three stations.

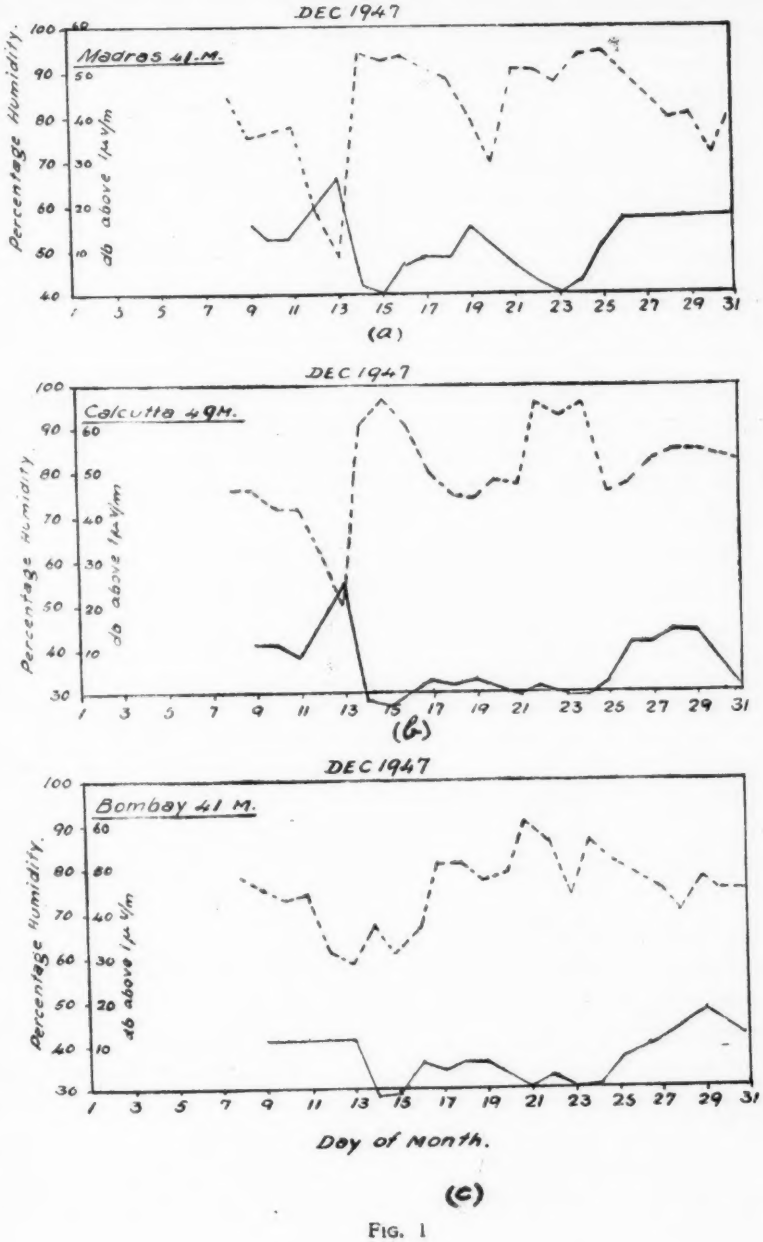
DEC 1947
Madras 41 M.
Percentage Humidity.
db above 1 μ v/m
(a)
DEC 1947
Calcutta 49 M.
Percentage Humidity.
db above 1 μ v/m
(b)
DEC 1947
Bombay 41 M.
Percentage Humidity.
db above 1 μ v/m
Day of Month.
(c)

FIG. 1

However, without anticipating the explanation of the mechanism by which the attenuation may take place, the following points may be noted:

1. The propagation is along the Ionosphere and the waves received may be either by a single reflection at the Ionosphere (*i.e.*, single hop), or by a series of reflections (multihop). In any case the wave has to pass through considerable distances in the atmosphere before incidence on, and after reflection at, the Ionosphere.

2. The attenuation of the signal may be due to absorption in the moisture-laden atmosphere or by the production of absorbing layers which bring about the attenuation, while the wave is passing through these regions. The production of such a region may be facilitated by the moisture content of the atmosphere.

To test this view-point an attempt has been made to see whether there is any correlation between the percentage humidities in the atmospher and the variation of the field strengths observed. The relative humidities were obtained from the Daily Weather reports and are plotted with dotted lines in figure 1.

The shortest line from Madras to Waltair lies over the sea and observations are not available along this line. Hence the humidities at places on the east coast are taken as representing the value along this route. For the Calcutta-Waltair route the observations from places along the route are available and their averages are taken as truly representing the state of the intervening atmosphere with regard to its water vapour content. The route from Bombay to Waltair lies over varied territory and the observation stations are not distributed along this route. Therefore the observations at stations near the Bombay and Waltair ends are taken, averaged and plotted in the graphs.

The dotted line curves in the figure represents the mean relative humidities in percentages along the routes averaged as indicated above.

Since the observations taken during the months of November 1947, January 1948 and April 1948 are not complete, the curves for these months are ommitted here.

February 1948

The curves showing the daily means of intensities of signals received from the Madras, Bombay and Calcutta stations are shown in Fig. 2. The curves for this month present the following features:

1. The intensity of signals received from Madras station show a small decrease during the period from 10th February to the 14th instant. From

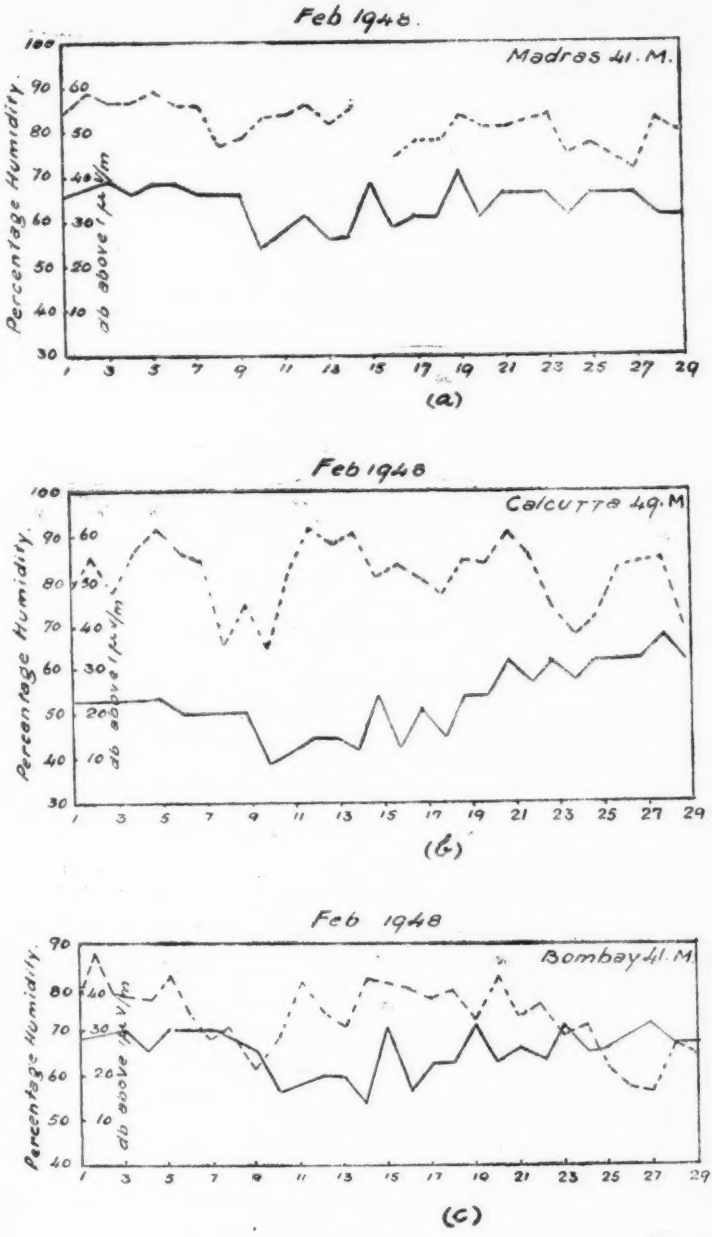
Feb 1948.
Madras 41. M.
Percentage Humidity.
db above 1 μv/m
(a)
Feb 1948
Calcutta 49. M
Percentage Humidity.
db above 1 μv/m
(b)
Feb 1948
Bombay 41. M
Percentage Humidity.
db above 1 μv/m
(c)

FIG. 2

16th to the 20th there are two slight decreases in intensities. But for this decrease, the intensities of the signals received from Madras are almost normal having field strengths approximately equal to 36 db above 1 μv/m.

2. The intensities of signals received from Calcutta are somewhat low during this period and increase during the last week of the month. As in the case of the signals from Madras, there is a decrease in signal intensity on the 10th of February, the decrease being more marked in this case. The intensity of signals from Madras falls from 36 db, *i.e.*, by 13 db, while the corresponding fall in intensity of the signals received from Calcutta is from 23 db to 7 db, *i.e.*, 16 db. The normal value of the signal strength from Calcutta is seen to be, from to graph, 31 db above 1 μv/m. Thus the signal intensity on 10th February was 24 db below the normal value, while in the case of the signals from Madras the signal intensity on the same date was 13 db below the normal value.

3. The signals received from Bombay show a normal intensity of 31 db above 1 μv/m. But it falls to 17 db on the 10th and the 16th instants and to 14 db on the 14th instant. The corresponding signal intensities in the case of signals from Madras and Calcutta on the same dates are 11 and 26 db and 14 and 31 db respectively. It may, however, be noticed that while the two stations, Calcutta and Bombay, show a decrease on the 14th instant and the 16th instant, Madras signals do not show any appreciable decrease in intensity.

The percentage humidities over the three routes are calculated as has already been outlined and are shown in Fig. 2 in dotted line curves. It may be noted from the curves that the percentage humidities over the Madras-Waltair route are fairly high, greater than 80% during this month except on the 15th and 16th instants and during the last week.

The average percentage humidities over the Calcutta-Waltair are also higher than 80% during the periods from the 1st to the 7th and from the 11th to the 22nd. It may also be noted from the curves that during these periods the intensities of signals received from Calcutta are generally low.

The average percentage humidities over the Bombay route range between 70% and 80% during most days of the month.

Leaving the 10th and the 16th instants out of consideration for the present, we may expect a general correlation again between the intensities of signals received at Waltair and the weather conditions, *i.e.*, in particular, the humidity and the amount of rainfall over the routes concerned.

March 1948

The corresponding curves for this month exhibiting the daily mean signal strengths on the 41 metre band are shown in Fig. 3. Observations

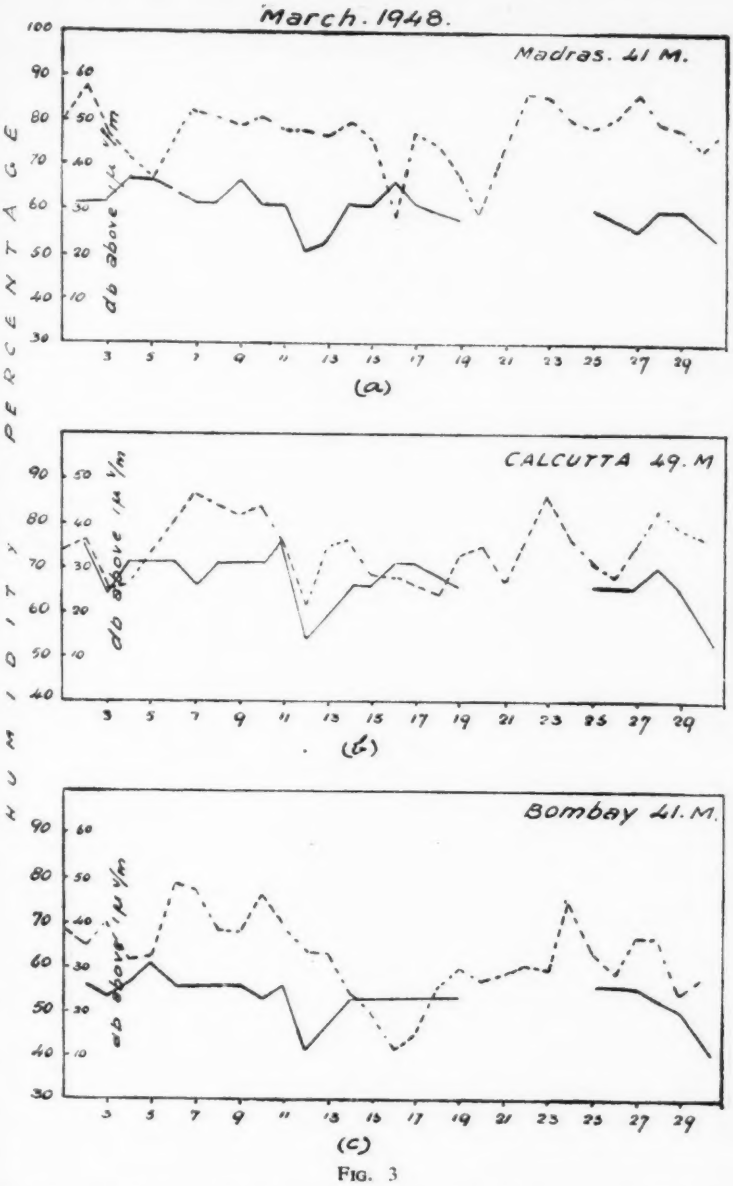

FIG. 3

during the period from 19th to 25th are rendered inaccurate by local disturbances.

The intensity of signals from Madras on the 41 m. band show an average intensity of 31 db above 1 μv/m., except for a slight decrease on the 12th and the 31st instants.

The Calcutta and Bombay signals also show an average field strength of 31 and 26 db respectively.

Signals from all the three stations exhibit a decrease in intensity on the 12th and the 31st instants. Signals from Calcutta and Bombay show a further decrease in strength on the 3rd while the Madras signals retain their normal value.

Weather during this period

As in the case of previous months the percentage humidities are shown in the same Fig. 3 as dotted line curves.

The percentage humidities over the Madras-Waltair route vary between 75% and 80%. The humidity has a value above 80% only for a day In a similar way, the humidities over the Calcutta and Bombay routes are also generally low. Occasionally they shoot up in values like 80-85% in the case of Calcutta and 75-79% in the case of Bombay.

May 1948

The most striking feature in the curves representing the daily mean signal strengths for the months of May is that the intensity of the Calcutta and Bombay signals are abnormally low after the 5th instant, reaching values as low as less than 1 μv/m. This tendency persists till almost the end of the month when the signal intensity rises up to a fairly high value but lower than the normal value.

Madras signals show a general low intensity after the 5th instant but are much stronger than the Bombay and Calcutta signals. There are two pronounced reductions in the strength of the signals received from all the three stations, on the 6th and the 13th instants. The signals from Calcutta and Bombay were so feeble that they could not be received on the 6th inst., while the signals received from Madras show a decrease from 31 db to 5 db. Again on the 13th, the Bombay and Calcutta signals show abnormally low values.

Weather during this period

The average percentage humidities are shown as dotted line curves in Fig. 4, for the month of May over the three routes. These values are normal throughout the month except for sporadic increases, and range between 60% and 80 %.

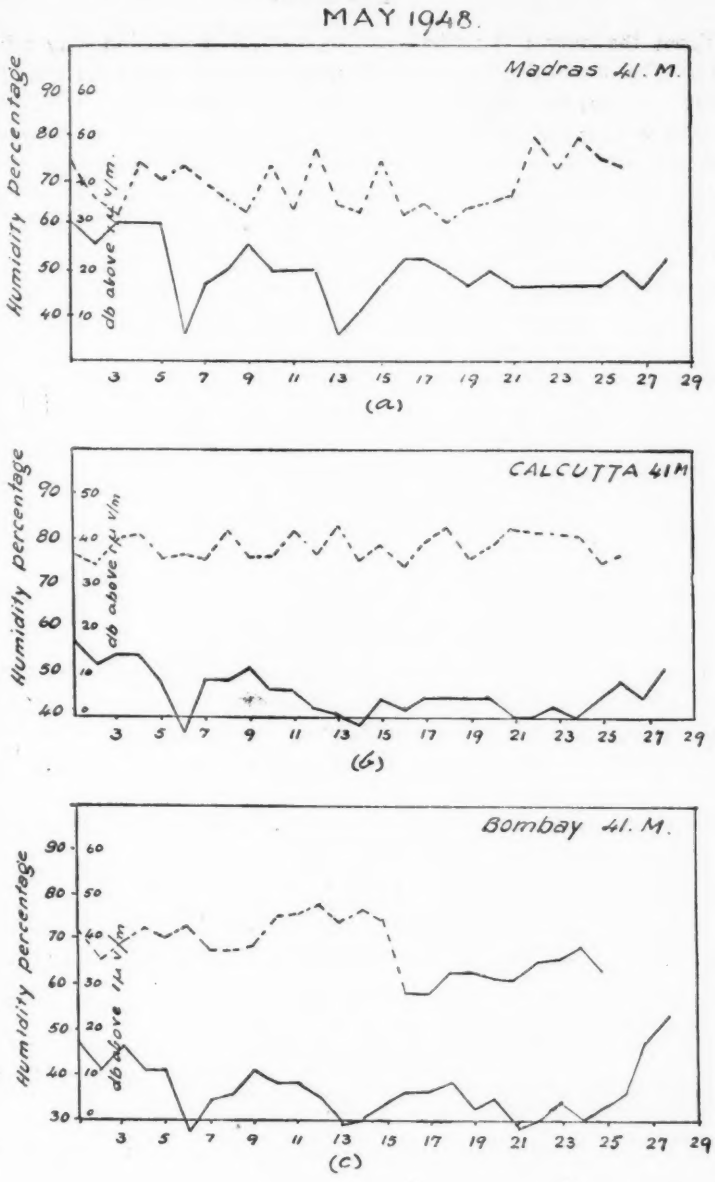
MAY 1948.
Madras 41. M.
Humidity percentage
db above 1 μ V/m
(a)
CALCUTTA 41M
Humidity percentage
db above 1 μ V/m
(b)
Bombay 41. M.
Humidity percentage
db above 1 μ V/m
(c)

FIG. 4

Discussion

From the curves described earlier, certain conclusion may safely be drawn. The curves for December show clearly that during the period when weather has been wet over a wide area, there is a definite correlation between the water vapour content in the atmosphere along the path of the wave and the signal intensities. Further, whenever the relative humidity rises above the value of 90% there is a large decrease in the signal strength. At the same time the recovery of the signal coincided with the reduction in the relative humidity of the atmosphere.

While this conclusion is so forcibly made to bear on us from a study of the curves for December, the curves for February, at first sight, appear to indicate that the above conclusion is not valid for the month of February. A closer examination, however reveals a very important feature. A definite correlation between the field strengths and moisture content of the atmosphere is seen as far as Calcutta signals alone are concerned, while no such thing is observed with the signals from the other two stations. It will further be noticed that the humidity in Fig. 2 (*b*) rose above 90%. they are lower in value in Figs. 2 (*a*) and 2 (*c*). Isolated rise of humidity to 90% does not appear to bring about the decrease in field strength. It is only when the moisture-laden condition of the atmosphere continues for a considerable period that the effect is noticed.

The curves for December show that almost every large change observed in field strength is accompanied by a corresponding change (increase or decrease as the case may be) of the water vapour content of the atmosphere. However, every change in one of the quantities is not always accompanied by a corresponding change in the other. The February curves show conclusively that this correlation is noticed only during a period of continuous wet weather along the route.

The curves for March and May bring out another important feature: that the field strength is not in the least affected by the humidity so long as it does not go above a limit which may be fixed round about 85%.

It may, therefore, be concluded that the study of the curves shows that:

1. During the wet season there is a definite relationship between the field strength of the received signals and the percentage humidities in the atmosphere along the path of the wave.

2. Further, these effects are more pronounced when the percentage humidities are round about 85%.

3. In cases where the humidities are much lower, there appears to be no correlation between the two quantities.

It will now be interesting to see in what way the presence of moisture in the atmosphere can bring about a reduction of field strength.

Several observers, Mitra and Bhar (1936), Colwell and Friend (1936), and Watson Watt, Wilkins and Bowen (1937), noticed radio pulse echoes from still smaller heights in the troposphere ranging from 5 to 50 km. It was pointed out by Mitra (1936) that this new region is quite distinct from the absorbing non-deviating region in the E-layer and that if echoes have actually come from well within the troposphere, it is doubtful if they were due to the Eccles-Larmor mechanism, for the necessary high degree of ionisation, if it existed, could scarcely have been missed in the aeroplane and balloon observations. He also suggested that this may be named the C-region.

Sayers (1938), by studying the values for the conductivity of the lower troposphere at heights up to 20 km. from the automatic records of stratospheric flights, found a close agreement between the theoretical curve and the experimental results. He finds, however, no indication there of the existence at any height below 20 km., of a region of sufficient ion density to reflect radio waves to any appreciable degree.

Colwell and Friend (1939) pointed out that medium and short radio waves in the troposphere could be reflected at the interface between air masses. To confirm this theory, they sent up an aeroplane which took reading of the air temperatures at different heights directly over the Radio Station while they were measuring the height of the reflecting layers by means of the pulse method. This was the first direct comparison between the two methods and they found that the agreement was perfect.

Another type of explanation suggested by Nasilov (1939) from a study of the weather maps for those days on which the 89 cases of severe fading reported by the Bureau of Standards for 1937, took place. This led him to the conclusion that fading could have been produced by the appearance of zones of condensation and that there is not sufficient justification for attributing it to solar activity.

Piddington (1939), suggested that the scattering of radio waves in the lower and middle atmosphere were due to scattering particles rather than to reflecting strata and that water vapour molecules were the more likely scattering agents, rather than electrons or heavy ions.

Appleton and Piddington (1939) suggested that the echoes from the troposphere were not necessarily due to ionisation, as this will involve high

values of conductivity but might probably be caused by other atmospheric discontinuities constituting what may be termed the B-region. Clouds would be effective as reflectors when situated above a point some distance from the transmitter.

Heightman (1949) however found variations of received signal strengths on a frequency of 3·6 Mc/s, and effects which could be attributed to the troposphere. Pickard and Stetson (1949) have attempted to correlate signal strength variations with temperature, atmospheric refraction, including pressure and humidity factors, and with wind direction, at frequencies from the broadcast band to 10 Mc/s.

There is, therefore, general agreement that the echoes observed are not due to ionised reflecting strata as this will mean regions of high conductivity which have been shown not to exist. The other possibilities are:

1. reflections at the interface between air masses,
2. reflections from clouds and
3. scattering by zones of condensation, water vapour molecules and heavy ions.

All these possibilities are connected with the existence of large quantities of water vapour extending up to considerable heights of the atmosphere. Brunt (1944) points out that we may regard the atmosphere as consisting of water vapour only as far as radiative effects are concerned and that the equilibrium of the temperature distribution in the atmosphere is mainly determined by the water vapour content.

Woolley (1947), while discussing the radiative equilibrium in the ionosphere, points out how, at lower levels, water is the most important factor and how profoundly it affects the temperatures in the Ionosphere. He suggests that the fact that the temperature in the F_1-region is considerably lower than the temperature of the F_2-region, may well be due to an appreciable water vapour population in the lower region.

It is, therefore, possible, that surfaces of discontinuity may be easily produced at different heights in the lower and middle atmosphere by the varying water vapour populations. In a similar manner large quantities of water vapour in the atmosphere may greatly facilitate the formation of clouds and zones of condensation.

The percentage humidities in the graphs presented earlier refer only to the ground observations. It is assumed that when large percentage humidities exist at ground level over large areas and for considerable periods, the vertical distribution of water vapour in the atmosphere will also be

affected in a similar manner. The variations of humidities at ground level may be taken as indicative of similar variations at higher levels.

In the present investigation a large reduction in signal strength was noticed when the relative humidities at ground level rose above 85%, during a period of continuous wet weather over a considerable area along the route of the wave between the transmitter and the receiver. Further, every major change in the humidity was accompanied by a corresponding change (increase or decrease as the case may be) of the signal strength. The signal strength returned to normal when the relative humidities were considerably reduced and no correlation could be found between the two quantities during the season of dry weather. It is now easy to see how this reduction in field strength is brought about.

We may picture the wave passing through the surfaces of discontinuity with reduction in intensity due to the loss of energy that is returned groundwards. This returned energy becomes useless for the purposes of long distance propagation as the reflection occurs at very low levels, and the energy associated with these is very small as the reflection coefficients are low.

Energy may also be lost by reflection at clouds or by zones of condensation or directly by water vapour molecules. Considering multihop transmission between the transmitter and the receiver, this reduction may take place a large number of times and the received signal intensity may be considerably reduced during this process. The amount of energy lost and the consequent reduction of signal strength will become great when the water vapour populations are large, *i.e.*, with large relative humidities of the atmosphere.

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RAMAN SPECTRUM OF FLUORSPAR AND ITS TEMPERATURE VARIATION

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1. Introduction

Fluorspar crystallises in the cubic system, the space group being O_h^5. The structure is made up of three interpenetrating face-centred lattices two of which are of fluorine atoms and the third of calcium atoms. It can be considered as a unit cube of calcium atoms in which the fluorines are situated at the body centres of eight small cubes formed by joining the mid-points of the edges of the unit cube. Every calcium atom is surrounded by eight fluorines and every fluorine by four calciums.

As specimens of fluorspar were readily available, it was one of the solids with which the earliest attempts to record a Raman spectrum was made. Nisi (1929) tried to obtain the Raman spectrum of fluorspar using λ 4358 radiation of the mercury arc as exciter, but failed to get any effect. A little later, the employment of a more powerful technique of excitation, namely the use of the λ 2536 resonance radiation enabled Rasetti (1931) to successfully record the spectrum of fluorspar. It exhibited a single line with a frequency shift $321 \cdot 5$ cm.$^{-1}$ This frequency represents the fundamental vibration of the fluorspar structure, *viz.*, the mode in which the two fluorine lattices oscillate against each other, the calcium lattice being at rest. This mode, according to the usual selection rules, should be active in the Raman effect. Rasetti, however, identified the observed Raman shift with the reststrahlen frequency of fluorspar appearing at 31 μ.

The author has re-examined the Raman spectrum of fluorspar using the Rasetti technique and has confirmed the appearance of the Raman line at $321 \cdot 5$ cm.$^{-1}$ Using a crystal of calcium fluoride of size $2 \cdot 5 \times 2 \cdot 5 \times 2 \cdot 5$ cm. and the medium quartz spectrograph, exposures of about six days failed to record any Raman line other than the one at $321 \cdot 5$ cm.$^{-1}$

2. Work at High Temperatures

In order to study the temperature variation of the Raman frequency of fluorspar, a crystal of fluorspar in the form of a polished plate $2 \cdot 5$ cm.

× 2·0 cm. and 0·8 cm. thick was used for this study. A casing of brass 3·0 cm. × 2·5 cm. × 1·1 cm. was made for holding the crystal. A rectangular aperture measuring 1·0 cm. × 0·8 cm. was made in one of the sides of the casing for the purpose of illuminating the crystal. The whole of the outside of this casing except for the window was covered with a thin sheet of mica and was then closely wound with strip heating wire. A coating of alumina mixed in sodium silicate was applied over the windings for the purpose of insulating them. When this coating had dried, a plane-parallel fused quartz plate was fixed on the window and the furnace was then wrapped with an aluminium foil in order to reduce loss of heat by radiation. A slit measuring 0·15 cm. × 1·0 cm. was made in the middle of the front end of the casing. The junction of an iron-constantan thermocouple was placed in direct contact with the crystal but thermally insulated from the inside surface of the metal casing. The furnace was fed by a battery of accumulators, the current being adjusted by a rheostat. It was necessary to prepare a schedule of the maximum steady temperatures attained with various known currents through the heating coil of the furnace with the crystal in position. This was accordingly done in a preliminary experiment. The light scattered by the crystal was focussed on the slit of the spectrograph by means of a quartz lens. The slit width used was 0·02 mm. and all the exposures were of three hours duration. The spectra were recorded on Ilford Selochrome plates and each spectrum was accompanied by an iron-arc spectrum superposed on it at its centre for comparison. During an exposure the temperature of the crystal was maintained constant by adjusting the current through the furnace. At low temperatures the furnace maintained a fairly steady temperature, but frequent adjustments were necessary at higher temperatures. The negatives were finally measured under a Hilger cross-slide micrometer and the frequency shift of the observed Raman line was calculated. To measure the width of the Raman line at different temperatures, the spectrograms were micro-photometered. From the micro-photometer records, the width of the line at half intensity was estimated.

3. Results

Fig. 1 (*a*) on Plate I is a reproduction of the Raman spectrum of fluorspar taken with the large E1 quartz spectrograph. The spectrum exhibits only a single intense Raman line. The most interesting feature is the extraordinary breadth of this line. This was not pointed out by Rasetti. The frequency shift and width of the line at 40° C. as measured from this spectrogram are 321·5 cm.$^{-1}$ and 8·7 cm.$^{-1}$ respectively. The value obtained by Rasetti for the frequency shift is 321·5 cm.$^{-1}$

TABLE I. *Temperature Variations of the Raman Line of Fluorspar*

Temperature °K	Position	Shift cm.$^{-1}$	Width at half intensity cm.$^{-1}$
313	321·5	0	8·7
317·5	321·3	0·2	8·7
345·8	319·3	2·2	10·0
402·5	317·4	4·1	12·7
465·8	315·0	6·5	14·9
494·7	313·7	7·8	15·9
526·9	312·6	8·9	17·0
559·5	312·2	9·3	20·8

Figs. I (*b*), (*c*) and (*d*) in Plate I represent the spectrograms taken at 44·5° C., 161·3° C. and 286·5° C. The measured variations in position and breadth of the Raman line are given in Table I. The line has an appreciable width even at room temperature. As the temperature is raised, the frequency shift of the line diminishes and the width increases, the increase in width being of the same order of magnitude as the displacement in its frequency shift. The temperature variations in the frequency shift and width of the line are graphically represented in Fig. 2. It is seen from the figure that the temperature-width and the temperature-frequency shift

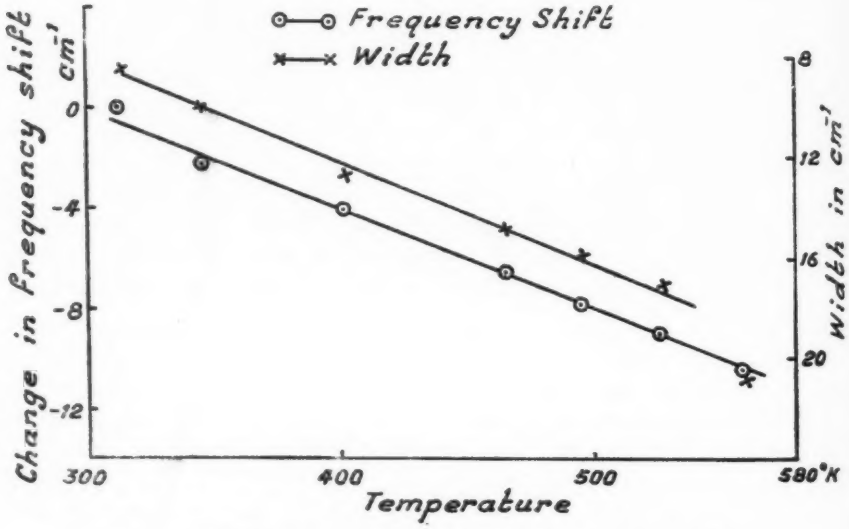

FIG. 2. Temperature dependence of frequency shrift and width of the Raman line of fluorspar

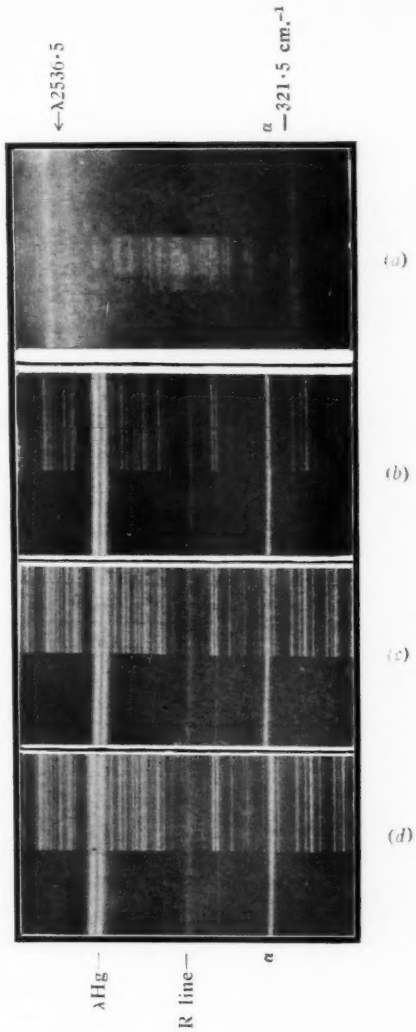

FIG. 1. (*a*) Raman spectrum of fluorspar taken with a E1 quartz spectrograph.

(*b*), (*c*) and (*d*) Raman spectra taken with a medium quartz spectrograph with the crystal kept at 44·5°C, 161·3°C. and 286·5°C.

curves are similar in shape showing thereby that the variations of frequency shift and width of the Raman line with temperature are closely related to each other. Similar observations have already been reported by Narayanaswamy (1947, 1948) for the Raman lines of calcite, quartz and barytes.

The mean proportional change in the frequency, namely $-\frac{1}{\nu}\frac{d\nu}{d\mathrm{T}}$ which is denoted by χ has been evaluated. For the temperature range 313° to 559·5° K., χ has a mean value of 118×10^{-6}. This is of the same order of magnitude as the χ value for the lattice lines of barytes observed by Narayanaswamy (1948). The relative change of frequency of the Raman line with relative change of volume which is expressed as γ_ν:—

$$\left[\gamma_\nu = -\frac{\Delta\nu}{\nu}\frac{\mathrm{V}}{\Delta\mathrm{V}} = -\frac{d\nu}{d\mathrm{T}} \cdot \frac{1}{\nu}\frac{1}{3\alpha_l}\right],$$

where α_l = coefficient of linear expansion), has also been evaluated, over the temperature range 313° to 559·5 ° K.

Mean value of $\gamma_\nu = 1 \cdot 7$.

The value of α_l was taken from the measurements of the author (D. C. Press, 1949). The mean value of the Gruneisen constant γ is equal to 1·9. Because of the finite width of the Raman line of fluorspar and consequent error in the measurement of $\Delta\nu$, it is too premature to attach any significance to the difference in the calculated values of γ_ν and γ.

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman for the loan of the fluorspar crystal and also to Prof. R. S. Krishnan for valuable discussions.

Summary

Using the λ 2536 Hg resonance radiation as exciter, the Raman spectrum of fluorspar has been investigated over the range of temperature from 313° K. to 559° K. The spectrum exhibits a single Raman line with a frequency shift 321·5 cm.$^{-1}$ at 313° K. which decreases to 312·2 cm.$^{-1}$ at 559° K. The width of line increases from 8·7 cm.$^{-1}$ to 20·8 cm.$^{-1}$ over the same range of temperature. The temperature-frequency shift and the temperature-width curves are similar in nature.

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ON AN ABSOLUTE CONSTANT IN THE THEORY OF TAUBERIAN SERIES : POSTSCRIPT

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Prof. R. P. Agnew has kindly sent me offprints of his paper " Abel transforms and partial sums of Tauberian Series ", *Annals of Mathematics*, Vol. 50 (1949), pp. 110–117, which seems to have been written earlier, but published later, than my paper appearing in the *Proceedings of the Indian Academy of Sciences*, Vol. 28 (1948), pp. 537–44. The latter paper proves, besides a generalization of a theorem of Prof. Agnew in the *Duke Mathematical Journal*, Vol. 12 (1945), pp. 27–36, the two main results of his later paper without, however, stating them as separate theorems. In fact, the relation (3·9) of my paper, in conjunction with the relation (3·5) from which it issues, establishes

Theorem A. *Suppose that*

$$F(s) = \sum_{\nu=1}^{\infty} a_\nu e^{-\lambda_\nu s} \ (s > 0), \ 0 = \lambda_0 < \lambda_1 < \lambda_2 < \ldots, \ \lambda_n \to \infty;$$

$$\lambda_n - \lambda_{n-1} = O(1), \ n \to \infty \ ; \ \frac{\lambda_n \mid a_n \mid}{\lambda_n - \lambda_{n-1}} < K, \ n = 1, 2, 3, \ldots;$$

$$A(x) = \sum_{\lambda_\nu \leqslant x} a_\nu, \quad \tau > 0.$$

Then

$$\limsup_{s \to +0} \mid A(\tau/s) - F(s) \mid \leqslant \mathrm{P}(\tau) \limsup_{n \to \infty} \frac{\lambda_n \mid a_n \mid}{\lambda_n - \lambda_{n-1}}, \tag{1}$$

$$\limsup_{u \to \infty} \mid A(\lambda_n) - F(\tau/\lambda_n) \mid \leqslant \mathrm{P}(\tau) \limsup_{n \to \infty} \frac{\lambda_n \mid a_n \mid}{\lambda_n - \lambda_{n-1}}, \tag{2}$$

where

$$\mathrm{P}(\tau) = \gamma + \log \tau + 2 \int_{\tau}^{\infty} t^{-1} e^{-t} \, dt,$$

γ being Euler's constant.

It is the case $\lambda_n = n$ of the above theorem that forms the subject of Prof. Agnew's later paper. By following his procedure and applying a result of his, *Annals of Mathematics, loc. cit.*, Lemma 3·1, to

$$A(\tau/s) - F(s) = \sum_{\nu=1}^{\infty} \beta_\nu(s) \, x_\nu$$

where $\beta_\nu(s)$, $\nu = 1, 2, \ldots$ is a real sequence such that

$$\lim_{s \to +0} \sum_{\nu=1}^{\infty} |\beta_\nu(s)| = \mathrm{P}(\tau), \quad \lim_{s \to +0} \beta_\nu(s) = 0 \ (\nu = 1, 2, \ldots),$$

and

$$x_\nu = \frac{\lambda_\nu a_\nu}{\lambda_\nu - \lambda_{\nu-1}},$$

we can at once complete Theorem A by means of

THEOREM B. *In* (1) *and* (2), *of Theorem A*, $\mathrm{P}(\tau)$ *is the best constant in the sense that there is a real series* Σa_ν *such that*

$$0 < \limsup_{n \to \infty} \frac{\lambda_n |a_n|}{\lambda_n - \lambda_{n-1}} < \infty,$$

and (1), (2) *reduce to equalities.*

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